THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

(ZHURNAL OBSHCHEI KHIMII)

Volume XXVII, No. 10

October, 1957

(A Publication of the Academy of Sciences of the U. S. S. R.)

IN ENGLISH TRANSLATION

Copyright, 1958

CONSULTANTS BUREAU, INC.
227 West 17th Street
New York 11, N.Y.

Printed in the United States

	Domestic	Foreign
Annual Subscription	$90.00	$95.00
Annual Subscription for libraries of non-profit academic institutions	30.00	35.00
Single Issue	10.00	

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

JOURNAL OF GENERAL CHEMISTRY OF THE USSR IN ENGLISH TRANSLATION

October, 1957

TABLE OF CONTENTS

	Page	Russ. Page
Fundamental Trends and Results of the Development of Chemistry in the USSR in the Last Forty Years. N. A. Domnin	2661	2609
Acetylene Derivatives. 187. Hydration of Diacetates of Acetylenic γ-Glycols. Synthesis of Unsaturated α-Acetoxyketones. III. I. N. Nazarov and S. G. Matsoyan	2676	2629
Geometric Isomerism of Δ^3-Tetrahydrotolualdehyde. I. N. Nazarov, G. P. Kugatova and V. V. Mozolis	2682	2635
Ethylene Sulfide in the Synthesis of Heterocyclic Compounds with Two Hetero-Atoms. III. 3-Arylthiazolidones-2 From N-(β-Mercaptoethyl)arylamines. Yu. K. Yuryev and S. V. Dyatlovitskaya	2689	2644
Investigation in the Field of the Synthesis of Organosilicon Compounds. III. Study of the Direct Synthesis of Methylchlorosilanes. A. L. Klebansky and V. S. Fikhtengolts	2693	2648
New Methods of Synthesis for the Esters of Polyene Carboxylic Acids. I. I. K. Saricheva, G. A. Vorobyeva and N. A. Preobrazhensky	2698	2653
Synthesis of 2,3,6-Trimethyl-2,6,8-undecatrien-10-one (Pseudoirone). II. I. K. Saricheva, G. A. Vorobyeva and N. A. Preobrazhensky	2707	2662
The Chemical Structure of the Hydrocarbon $C_{12}H_{14}$ and the Synthesis of New Phenylated 1,3-Diene Hydrocarbons. VII. V. I. Esafov	2711	2667
The Reaction of Chloroalkylalkyldichlorosilanes With Aromatic Compounds in the Presence of $AlCl_3$. E. A. Chernyshev, M. E. Dolgaya and Yu. P. Egorov	2718	2676
Compounds With Two Electron Donor Systems. II. Color Phenomena in Derivatives of N-(Phenyl-glycyl)-o-(3-nitrobenzoyl)-p-aminophenol. E. A. Smirnov	2724	2682
The Reaction of Alkylhalosilanes With Trialkylsilanes. B. N. Dolgov, S. N. Borisov and M. G. Voronkov	2733	2692
Catalytic Alkylation of Phenol With Methyl Alcohol. I. N. Samsonova	2738	2697
Synthesis of Aromatic Compounds of Antimony. IX. Preparation of Antimonioaromatic Compounds Using Antimony Pentachloride and Phenylhydrazine. A. B. Bruker	2741	2700
Tautomerism of Salts of Aminoazo Compounds. I. N. Zhmurova	2745	2704
Reaction of Halogen Exchange in α-Chloro Sulfides. K. A. Petrov and G. A. Sokolsky	2751	2711
Reaction of Organosilicon Compounds With Phosphorus Chlorides. A. P. Kreshkov and D. A. Karateev	2755	2715
Catalytic Dehydrogenation of Isopentenes Into Isoprene. Yu. N. Usov, E. V. Skvortsova, N. I. Kuvshinova and L. A. Elovatskaya	2761	2721

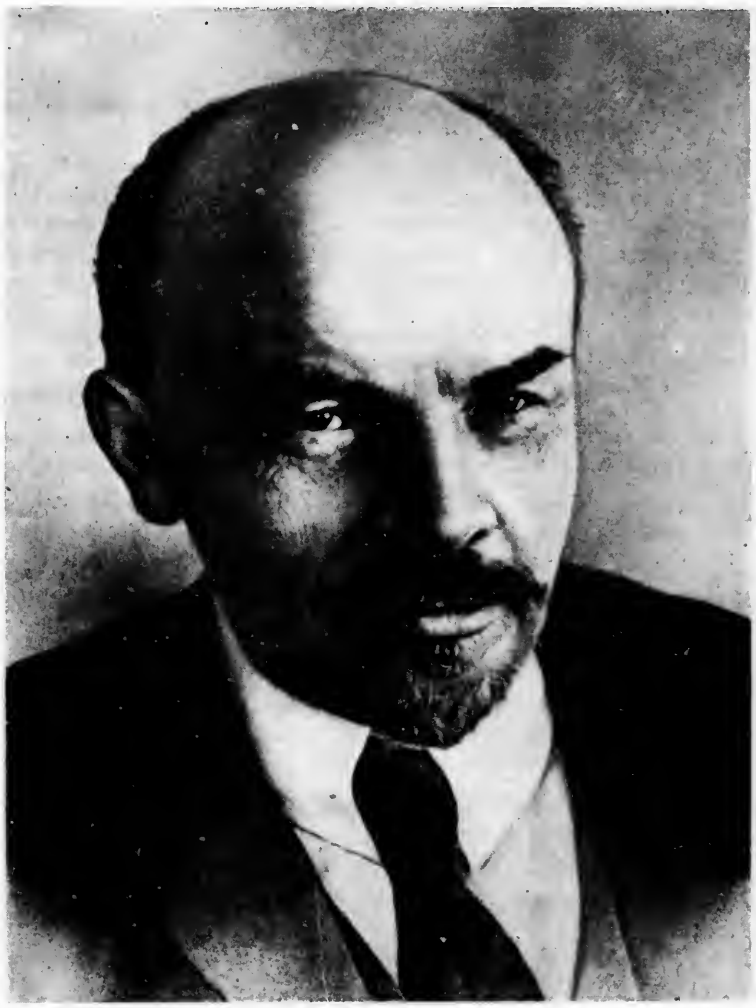
(continued)

TABLE OF CONTENTS (Continued)

	Page	Russ. Page
Acetonation of Higher Aliphatic Dihydroxy Acids. P. A. Artamonov	2766	2726
Imines of Di- and Polyketones. II. Trisindandione. G. Ya. Vanag and G. Ya. Dubur.	2769	2729
Imines of Di- and Polyketones. III. Benzalindandione. G. Ya. Vanag, E. I. Stankevich and E. Ya. Gren	2773	2733
Iodonium Derivatives of β-Diketones. I. Reactions of Dimedon With Iodosobenzene. E. Gudrinietse, O. Nieland and G. Vanag	2777	2737
Spectroscopic Study of 3-Acylpyrazoles. N. K. Kochetkov and Ivan Ambrush	2781	2741
Synthesis of Aryl β-Acylvinyl Sulfones and Aryl β-Acylvinyl Sulfoxides. N. K. Kochetkov and V. N. Vinogradova	2785	2745
Allylic Rearrangements. XIX. Reactions of Organomagnesium Compounds and Diethyl Sodium Phosphite With Isomeric Isoprene Hydrochlorides and Methoxychloroisohexenes. A. N. Pudovik and I. V. Shergina	2789	2750
Dealkylation of Isomeric Tributenyl Phosphites with Hydrogen Chloride. A. N. Pudovik	2794	2755
Problems in the Structure of Cotarnine Derivatives. III. Structure of "Hydrocotarnineacetic Acid". Denesh Beke, Kalman Kharshani and Iene Kereshi	2798	2760
Problems in the Structure of Cotarnine Derivatives. IV. Structure of Products of the Condensation of Cotarnine With Acetone. Denesh Beke and Kalman Kharshani	2804	2767
Reactions of Free Radicals in Solutions. XIII. Study of the Mechanism of the Inhibiting Effect of Quinones on the Initiation of Polymerization. B. A. Dolgoplosk and G. A. Parfenova	2810	2773
Investigation of the Sulfonation Reactions. XLIII. Sulfonation of Benzene to Disulfonic Acids. A. A. Spryskov and S. P. Starkov	2816	2780
Halogenation of Aromatic Silanes. V. Preparation and Properties of Chlorobenzyl- and Chloro-p-tolyltrichlorosilanes Containing Chlorine Atoms in the Aliphatic Part of the Radical. G. V. Motsarev and A. Ya. Yakubovich	2822	2786
Sulfonic Acids of Sulfones as Side Products in Sulfonation Processes. IV. Investigation of the Possibility of Polarographic Determination of Sulfonic Acids of 4,4'-Dimethyldiphenyl Sulfone, 4,4'-Dichlorodiphenyl Sulfone and 2,2'-Dinaphthyl Sulfone. A. P. Shestov and N. A. Osipova	2826	2790
Preparation of Difluoroketene and its Polymer. N. N. Yarovenko, S. P. Motornyi and L. I. Kirenskaya	2832	2796
A Study of the Mechanism of the Reaction of Tertiary Amines With Esters. S. V. Vitt and R. V. Kudryavtsev	2835	2799
Reaction of the Simplest Olefins With Aqueous Solutions of Formaldehyde and Acetaldehyde. M. I. Farberov, Ya. I. Rotshmein, A. M. Kutin and N. K. Shemyakina	2841	2806
Trichlorophosphazosulfonenitroaryls and Their Hydrolysis Products. A. V. Kirsanov and N. G. Feshchenko	2852	2817
The Neutral Form of a Diazo Compound. I. V. Grachev, G. G. Gusev and D. Z. Zavelsky.	2856	2820
The Reaction of a Hydrochloric-Acid Solution of Iodine Trichloride With Certain Unsaturated Compounds. Ya. A. Fialkov and F. E. Kagan	2865	2830

TABLE OF CONTENTS (Continued)

	Page	Russ. Page
The Replacement of the Halogen Atom in Phenazine Halides by Methoxy, Hydroxy, Amino and Mercapto Groups. V. P. Chernetsky	2869	2833
The Synthesis of Substantive Dyes of the Biquinoline Series. L. N. Goldyrev.	2874	2837
Vinylation of D-Glucose and Its Acetone Derivative. I. B. I. Mikhantyev and V. L. Lapenko	2877	2840
5-Halofurylacrylic Acids and Their Derivatives. Z. N. Nazarova and M. I. Pimenova	2879	2842
Syntheses and Transformations in the Diarylurea Series. II. Synthesis of Chlorine-Substituted Diarylureas. D. F. Kutepov and N. S. Rozanova	2882	2845
Syntheses and Transformations in the Diarylurea Series. III. Synthesis of Fluorine-Substituted Diarylureas. D. F. Kutepov and N. S. Rozanova	2885	2848
Investigation of Carbonyl Derivatives of Benzene Using Spectrographic and Other Physicochemical Methods. III. Investigation of 1,3-Dihydroxy-4,6-diacetylbenzene and its Mono- and Di-Methyl Ethers. F. F. Cheshko and B. G. Distanov	2888	2851
Catalytic Condensation of Acetylene with Aromatic Amines. XXVI. Catalytic Condensation of Compressed Acetylene With Aromatic Amines in Vapor Phase. N. S. Kozlov and S. Ya. Chumakov	2894	2861
Synthesis of 1-(4'-Sulfonophenyl)-3-methylpyrazolone-5 From Diketene and 4-Sulfonophenylhydrazine. P. A. Levin	2900	2864
Condensation of Propylene Oxide With Some Aromatic Hydrocarbons. V. R. Likhterov and V. S. Etlis	2903	2867
Synthesis of α,β-Dimercaptopropionic Acid, Containing Radioactive Sulfur. A. B. Silaev, An. N. Nesmeyanov, V. M. Fedoseev and N. V. Kondakova	2907	2871
Synthesis of Diethylaminoethanol, Labeled With Radiocarbon C^{14} in One of the Ethyl Groups. L. B. Dashkevich	2910	2874
The Initiating Effect of Some Acyl Peroxides. K. S. Minsker and L. V. Stupen	2912	2875
The Thermochemistry of Substitution in the Aromatic Nucleus. I. The Heat Effect in the Sulfonation of Resorcinol. V. N. Kiselnikov and T. S. Kazas.	2914	2877
Synthesis Using Acrylonitrile. XXXII. Some Derivatives of Cyanoethylated α-Amino Acids. A. P. Terentyev and P. F. Butskus	2921	2884
Synthesis of Some Thiodialdehyde Acetals. S. M. Gurvich	2925	2888
Aminoacyl Derivatives of Nucleosides. 1. Synthesis of N_6-Aminoacyl and N_6-Peptide Derivatives of 3-β-D-Glucopyranosylcytosine. Z. A. Shabarova, N. I. Sokolova and M. A. Prokofyev	2928	2891
The Synthesis of Thiazolidone Derivatives of Biological Interest. VI. The Condensation Reaction of Monochloroacetic Acid and Thiosemicarbazide in the Presence of Aldehydes. E. V. Vladzimirskaya	2934	2898
The Representation of the Periodic System of the Elements. A. M. Vasilyev.	2938	2902
Letters to the Editor	2943	2907



FUNDAMENTAL TRENDS AND RESULTS OF THE DEVELOPMENT OF CHEMISTRY IN THE USSR IN THE LAST FORTY YEARS

N. A. Domnin

The fortieth anniversary of the October Revolution finds the Soviet nation successful in constructing a communist society.

The 20th session of the Communist Party of the Soviet Union has presented plans for the economic and cultural growth of the nation. The session emphasized that the chief problems in the development of the national economy of the USSR (on a basis of preferential development of heavy industry) are: continuous technical progress and increased productivity of work; further growth of all branches of national economy; a marked increase in agricultural production; and the consequent attainment of a decided advance in the material advantages and the cultural level of the Soviet Nation.

The USSR now plans to set up the conditions required for solution of the country's basic economic problems in the face of international competition; it plans to reach and surpass the greatest developments of capitalistic countries in per capita production.

Through planned progress and perfection of technology, the Soviet Union at its fortieth anniversary has attained a strong socialistic industry, based on great natural resources and many highly qualified workers.

The national economy shows steady progress. The Communist Party of the Soviet Union and its Central Committee will further this progress by uniting industry and construction to achieve the fullest use of the great natural reserves.

The decisions of the 20th session are a creative development of Marxist-Leninist teachings. They defend the basic position of Marxism-Leninism and also prepare the Party for the struggle against ignorance and stagnation in science and against worn-out dogmas by creative new generalizations.

The 20th session has encouraged the Soviet intelligentsia to aid the growth of Communism by improving the organization of scientific research. Soviet chemistry, along with the other branches of science, has taken part in the remarkable development of the past forty years. It has made new and far-reaching discoveries.

Even in pre-revolutionary times, Russia produced scientific scholars with world-wide reputations, including the famous chemists, M. V. Lomonosov, D. I. Mendeleev, A. M. Butlerov, and their many students who enriched the scientific world with their fundamental discoveries.

After the October Revolution, a particularly intense development of chemical science and industry began in the USSR. Even in the first years of Soviet rule, at the direction of V. I. Lenin, new institutes and laboratories for chemical research were founded by the great Russian scholars, N. S. Kurnakov, L. A. Chugaev, A. E. Pavrosky, N. D. Zelinsky, A. N. Bakh, V. I. Varnadsky, and others. These famous scientists inherited and developed the best traditions of Russian science and founded their own productive schools of chemistry.

We must mention a number of essential and characteristic features in the development of chemistry in the Soviet period. The most important was the clear tendency to reconstruct and make chemistry, as other branches of Soviet science, a concern of the whole country, by using measures organized and planned by the highest organs of State and Party. As a result, chemistry, as other sciences, became democratic and national in the first years of Soviet rule, for it began to serve the nation and the people who came from every group in the nation. Soviet rule created new conditions for the development of chemistry, set before it new goals and problems, and changed the scale, the tempo, the dimensions, and the character of its progress. Chemists, like all Soviet

scientists, saw clearly the need for combining theory with practical problems and questions, with industry, and with daily guidance from the Communist Party and the Soviet Government whose continuous care for the development and advance of Soviet science has had a decisive effect on the rapid advance of chemistry and chemical industry. The brilliant discoveries of Russian chemists, which had been chiefly theoretical, began to find practical use in stimulating industry, and the rapid development of industry in turn raised new questions and problems which greatly stimulated the further advance of theoretical chemistry. As a result, the combined development of theory and practice in chemistry permitted a unique advance for both chemistry and industry.

Developing and perfecting the plans of Lenin for the nature, path and advance, and character of Soviet science, the Communist Party constantly and successfully preserved his ideals and defended their purity. On this basis the Soviet Government has trained and educated many Soviet chemists.

As a result of this work by the Communist Party our Soviet chemists in the forty year period have advanced to a leading position in the world of chemistry. Our socialist chemical industry has attained a similar position.

One of the chief characteristics of chemistry in the Soviet period has been the rapid development of borderline fields such as physical chemistry and chemical physics, crystal chemistry and geochemistry, biochemistry and biogeochemistry, radiochemistry, etc. This period saw the perfection of the great discoveries of physics and chemistry which greatly changed and deepened our ideas of the nature of the atom and the elements, chemical compounds, and chemical bonds; it saw the rapid development of the electron and quantum theories, introduced the chemistry of the transuranium elements, etc. The Soviet period of the development of chemistry has been characterized by brilliant ideas on the structure of atoms and molecules and the mechanism of chemical reactions.

The intensive development of chemistry in these directions called for wide utilization of new and more perfect methods of physical and chemical investigation. In recent years chemistry has used with success many methods of contemporary physics: spectroscopy, x-radiography, electronic techniques, neutrons, magnetic resonance, etc.

Measurements of heats of combustion, heats of chemical reactions, and heat capacities permitted determination of important thermodynamic properties of substances – energy of formation, entropy, and free energy. These results permitted drawing conclusions of the structure of molecules and determination of the equilibrium constants of chemical reactions.

The development and use of quantum-chemical calculations led to the newest and most promising field – quantum chemistry, which gives a deeper and more exact idea of the nature of chemical bonds, interatomic distances, valence states of atoms, valence angles, and the form and structure of molecules.

Studies of the transitional, oscillatory and electron spectra of molecules permit determination of the energy levels of molecules and establish a connection between structure and molecular spectra. Measurement of dipole moments permits determination of the polarity of molecules and different atomic groups, and the final results make possible qualitative determination of the magnitude of the electrical charges in the molecule.

The method of labeled atoms has found wide use in chemical research; this makes possible the solution of a number of important questions and problems of contemporary chemistry and has already established new and significant relations between the structure and reactivity of molecules.

Soviet chemists and physicists have carried out original and important investigations in all these fundamental fields of chemistry. Extensive and detailed studies have been made of processes which occur under the influence of light (A. N. Terenin). Terenin discovered effects of photodissociation of the vapors of salts, worked out new optical methods for the study of photochemical processes which occur in complex organic molecules, and discovered methods of measuring the rate of reactions which proceed in layers of gas adsorbed on the surfaces of solids.

Great success has been attained in the study of the theory of oscillation spectra. As a result of broad studies in this field, a method was developed for calculating the oscillations of polyatomic molecules which established a relation between the structure and oscillation spectra of molecules (B. N. Stepanov, M. A. Elyashevich). An investigation of the phenomena of the optical activity of molecules was completed (M. V. Volkenshtein). Many investigations by Soviet chemists threw light on the dipole moments of a number of organic compounds (Ya. K. Syrkin, B. A. Arbuzov and others).

Studies were made on crystals composed of very densely packed atoms and from these the structures of linear and ring silicates such as tourmaline were determined (N. V. Belov and his students). Studies of the structures of crystals of inorganic substances (G. S. Zhdanov, G. V. Boky, etc.) were completed by x-ray analysis of a whole series of organic molecules (A. I. Kitaigorodsky).

Boron hydrides (B. V. Nekrasov) and the distribution of electron densities in metals (N. V. Ageev) were investigated.

With the help of x-ray and electron methods, the amorphous structure of cellulose and a number of its derivatives was established, leading to the study of the thermodynamic and mechanical properties of polymers and giving methods for estimating the flexibility of polymeric molecules (V. A. Kargin).

In recent years, theoretical studies in quantum chemistry have been carried out (Syrkin and others). The method of labeled atoms has permitted original experimental work on the equivalence of chemical bonds in nitrogen atoms of quaternary ammonium compounds (Syrkin) and phosphorus atoms which form pentaphenyl phosphorus molecules (G. A. Razuvaev). It has also been shown that in the case of the nitrogen atom the four covalent bonds are equivalent, and in the case of the phosphorus atom in pentaphenyl phosphorus all five bonds are equivalent; this agrees with conclusions made from the quantum theory of valence.

The theory of chain reactions has been very successfully developed (N. N. Semenov and his school). They discovered and worked out a quantitative theory of unbranched- and branched-chain reactions, in which had been observed a series of properties not explained by the classical ideas of chemical kinetics. They developed the theory of chain reactions on the walls and within a vessel, the theory of the upper and lower limits of a combustion chain, the limiting effects in a slow chain reaction, the theory of degeneration of side reactions and of explosions which occur by chain reactions.

Further studies have shown the formation in a number of reactions of free radicals – OH, CS, SO – and free atoms of hydrogen; the first kinetic investigations were made to study the separation of intermediate substances and their reactions which laid the foundation for experiments on the mechanism of complex reactions (V. N. Kondratyev). From these studies it was found that the relations between the structure of reacting molecules and their reactivities could be followed. The basic characteristics of the reactivity of a substance were found to be the value for its energy of activation and the rate constants of the elementary reactions. The study of catalytic effects had a wide and many-sided development (A. A. Balandin, S. Z. Roginsky, N. S. Kobozev, Semenov and others). Extensive studies were carried out in thermochemistry, and great use was made of the energy equations of crystal ionic lattices (A. F. Kapustinsky). From these equations, knowing the composition of the compounds and the ionic radii, it was possible to calculate directly the heat of formation of the crystal from its separate ions. A series of interesting studies cast light on the problem of the solvation of ions (K. P. Mishchenko, Kapustinsky, O. Ya. Samoilov, and others).

A series of studies was carried out to improve new calorimetric apparatus (M. M. Popov and others).

One of the most important parts of chemistry is the field of solutions, which has been extensively studied in the last forty years. It is true that Soviet chemistry was already prepared for further development, since the pre-revolutionary Russian chemists had made many such studies (Mendeleev, I. A. Kablukov, B. A. Kistyakovsky, L. V. Pisarzhevsky, D. P. Konovalov, M. S. Vrevsky and others). Of special value for the theory of solutions was the work of Mendeleev, who held that in solutions chemical reaction occurred with formation of compounds of variable composition between solvent and solute.

Kablukov and Kistyakovsky developed the idea of hydration of ions and thus reconciled the contradiction between chemical and physical theories of solution. Later studies in nonaqueous solutions showed chemical effects in these solutions (L. V. Pisarzhevsky, V. A. Plotnikov, V. A. Izbekov, Ya. A. Fialkov). It was shown that there was a close connection between electrical conductivity and the formation and decomposition of complexes in solution, and that in many cases the deciding factor was not the dielectric permeability of one of the components acting as solvent, but reaction between the components of the solution (M. I. Usanovich, M. A. Klochko, and others).

In the 1940's, the theory of ionic exchange was explained (B. P. Nikolsky); this development has continued in post-war years with special attention to one phase of the theory – a detailed study of the glass electrode. The technology of making glass electrodes has been developed, permitting measurement of hydrogen ion concentration in very wide limits and allowing automatic control of production processes. Nikolsky produced glass electrodes

with metallic properties which have found wide use in a number of special cases. A particular type of ion exchange is chromatography.

An original theory of acids and bases was developed (A. I. Shatenshtein, Usanovich, N. A. Izmailov). The study of phase equilibrium of gases at high pressure led to the discovery of the phenomenon of layering of gas mixtures (I. R. Krichevsky). The theory of dilute solutions of strong electrolytes was supplemented by ideas on the association of ions (V. K. Semenchenko).

The general thermodynamic theory of multicomponent heterogeneous systems was further developed. Important theoretical and practical results were obtained by working out the thermodynamics of ternary triphase systems. The scientific trends of the Russian thermodynamic school of Konovalov and Vrevsky were extended to the field of solution theory (A. V. Storonik).

There have been many investigations of electrochemical forces with study of the central problem of the nature of the potential difference between electrodes and the mechanism by which it occurs. In this connection there have been studies of the mechanism of electrode processes, surface effects, and the nature of polarization and electromotive force. (A. N. Frumkin, N. A. Izgaryshev, A. I. Brodsky and others.)

A systematic investigation was made of the kinetics of solution of metals in acids, an important part of the contemporary electrochemical theory of the reaction of metals with acids (Ya. V. Durdin, A. I. Shultin).

As part of the study of the corrosion of metals, an extensive investigation was carried out which led to a number of theoretically and practically important generalizations and results (Kistyakovsky, Izgaryshev, G. V. Akimov, N. D. Tomashov).

Great success was attained in the field of structure and properties of heterogeneous disperse systems and the processes which occur in them. The nature of lyophilic colloid systems was studied (A. V. Dumansky, N. P. Peskov) and a theory was worked out for the coagulation of lyophobic sols (A. I. Rabinovich) and the stability of aerosols.

The role of electrokinetic effects in electrodialysis of dilute solutions and suspensions was studied and a method was worked out for purifying water by electrodialysis (I. I. Zhukov). The theory of electrokinetic properties and structure of a number of capillary systems was developed and tested experimentally, and on this basis a method was proposed for purifying natural waters. A membrane was invented for dialyzers with almost unipolar penetrability (from ion-exchange adsorbents) (O. N. Grigorov).

A wide study was made of colloid systems resulting in fundamental changes in ideas on the nature and stability of solutions of hydrophobic colloids; this for the first time explained the definite role of chemical phenomena for their formation and stability (Kargin). These investigations found practical use in the study of ion exchange in soils, in working out methods for increasing the water saturation of sandy soils and in purifying colloidal solutions and precipitates from electrolytes by electrolysis. The theory of gel formation, swelling, and syneresis was developed (S. M. Lipatov). The physicochemistry of rubber and its structural changes during oxidation and vulcanization were investigated (B. A. Dogadky). Studies were made of adsorptive effects at the surface of molecules and their role in disperse systems (P. A. Rebinder, D. L. Talmud), as well as of structure formation in disperse systems, the mechanical properties of thixotropic structures, and the chemistry of adhesives (Rebinder). A theory was worked out for the coagulation of disperse systems by electrolytes and the binding together of solid particles (B. V. Deryagin). A method was found for dispersion and sedimentation analysis (N. A. Figurovsky).

The phenomena of adsorption were widely studied and the results served as a basis for purification of petroleum products. (L. G. Gurvich). Investigations were carried out in the field of adsorption of electrolytes from mixed solvents with a consideration of the action of molecular forces and the distribution of substances between two solvents (N. A. Shilov, L. K. Lepin). Numerous studies of adsorption were carried out by Shilov, M. M. Dubinin, Frumkin, and others.

Even in pre-revolutionary times N. S. Kurnakov developed the theory and method of physicochemical analysis and its application to the study of metals, salts, and organic systems. However, extensive studies in this field have developed only in the Soviet period. Kurnakov founded the world's greatest school of investigation of physicochemical analysis, which included a large group of his talented students (Ageev, V. Ya. Anosov, A. G. Bergman, A. T. Grigoryev, N. N. Efremov, S. F. Zhemchuzhny, Klochko, S. Z. Makarov, V. A. Nemilov, S. A. Pogodin, P. Ya. Saldau, N. I. Stepanov, I. V. Tananaev, G. G. Urazov, and others). The investigations of

the Kurnakov school developed the theory and method of physicochemical analysis with studies of metal, salt, and organic systems and natural minerals, salts, and ores.

It was found that by physicochemical analysis it was possible to study both homogeneous and nonhomogeneous systems composed of one, two, or a large number of simple or complex components. A quantitative study of the relations between composition or other factors of an equilibrium system and its physicochemical properties such as conductivity, hardness, viscosity, crystallization temperature, etc. was based on physicochemical analysis. Later, it was found that among the properties which could be studied by physicochemical analysis was the rate of transformation of a physicochemical system depending on its composition, and this began the kinetic method of physicochemical analysis (N. I. Stepanov, Kapustinsky, V. I. Nikolaev, I. I. Kornilov, M. B. Neiman and others).

Studies were carried out which led to the discovery of alloys with high electrical resistance(Zhemchuzhny, Nemilov, Pogodin, Kornilov). Alloys of the light metals magnesium and aluminum were studied (Pogodin, F. I. Shamrai, V. I. Mikheeva, D. A. Petrov and others). These studies permitted the development of light and ultralight alloys with great strength, which were needed for the tractor and aviation industries. Physicochemical analysis was widely used in inorganic chemistry, particularly in studying the chemistry of metallic alloys, aqueous salt solutions, silicates, etc.

The fundamental work of Kurnakov and L. A. Chugaev played a decisive part in developing the chemistry of complex compounds of the platinum metals, cobalt, nickel, etc. The chief scientific center for the study of the chemistry of complex compounds was the Institute of Platinum and Other Precious Metals, organized at the suggestion of Chugaev (1918). Here many studies were carried out of new complex compounds of platinum, rhodium, iridium, and palladium (I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinsky, N. K. Pshenitsyn, A. D. Gelman, and others).

The discovery and study of optically active complex compounds (Chernyaev) and the study of new forms of geometric isomerism (Grinberg, B. V. Ptitsyn) made possible the establishment of the stereochemistry of divalent platinum. The discovery by Chernyaev of the rule of the trans effect was very important in studying the nature of the complex compounds, and made it possible to develop further the synthesis of many compounds of platinum and other new compounds with specified properties.

Other important steps were the study of the chemistry of complex aluminum compounds (Plotnikov), molecular rearrangements of complex compounds (Nekrasov), the structure of hydrides and peroxides (A. I. Kazarnovsky), and the chemistry of silicates and binding materials (P. P. Budnikov).

Many very important studies were made by Soviet scholars on the structure of glass and the relation of properties of glass to composition (A. A. Lebedev, V. V. Vargin, K. S. Evstropyev, R. L. Myuller, I. I. Kitaigorodsky and others), heterogeneous equilibrium in silicated systems (D. S. Belyankin, N. A. Toropov, K. G. Kumanin, I. F. Ponomarev, G. V. Kukolev), and the theoretical and practical basis for making optical glass (I. V. Grebenshchikov, N. N. Kachalov, G.Yu. Zhukovsky).

Studying the theoretical basis for a number of metallurgical and technological processes (E. V. Britske, A. A. Baikov and co-workers) the investigators worked out new methods for getting concentrated and complex fertilizers (S. I. Volfkovich and others).

The development and perfection of methods for the analysis of minerals, ores, and rocks, and the chemistry of rare and scattered elements occupied many investigators (I. P. Alimarin, Yu. V. Morachevsky, and others). Methods of micro- and ultramicroanalysis, methods of analysis of the microquantities of minerals in slag and products of mineral synthesis, determined by successful micromethods, permitted establishment of field laboratories (Alimarin).

Along with the development of classical physical and chemical methods of qualitative and quantitative analysis there was a great development and expansion of new methods: spectroscopic, x-ray, polarographic, potentiometric, luminescent, electroanalytic, chromatographic, spot analysis (Tananaev), isotope distribution, and others. Analysis with organic reagents was very useful (there were a number of works which explained the theoretical side of this question (V. I. Kuznetsov, L. M. Kulberg).

In connection with the great industrial value of the rare, rare earth, and light metals, there was extensive study of the chemistry of these elements, methods for obtaining them in pure form, and their estimation and analysis in natural sources and industrial wastes. Soviet chemists performed important and valuable work in this field.

Experimental thermodynamic studies were carried out to explain the reason for the existence in nature of a definite, limited number of binary compounds. In the development of this work which was connected with deepening our understanding of the principles of the limit of symmetry and substitution, a method was developed for estimating the value of the enthalpy of formation of binary compounds (S. A. Shchukarev). This method was used successfully in studying the oxides and halides of subgroup elements.

At the time of the October Revolution, Russia had no radiochemistry as a science and only later did the Soviet government begin and develop this important field of chemistry and physics. At the present time the USSR has a powerful radiochemical industry which has worked during the Soviet regime to discover and extract the natural sources.

The development of radiochemistry began in our country in the twenties under the direction of the famous students of Chugaev, V. G. Khlopin, who obtained the first Soviet preparation of radium and, with Vernadsky, organized the Radium Institute (1922). In this and later years, investigations on radiochemistry were carried out widely and intensively in all important branches. Khlopin founded a scientific school which included his talented students, such as B. A. Nikitin, A. E. Polesitsky, A. P. Ratner, V. I. Grebenshchikova, and others. Khlopin discovered the law of distribution of radioelements between liquid and solid phases which played a great part in the separation of radioelements from dilute solutions. The distribution law was applied to systems in which the distributing component was isomorphous with the solid crystalline phase. The question of the mechanism of isomorphic substitution in forming mixed crystals was studied in detail and gave a classification of substances. Later, it was established that the application of Khlopin's law to the distribution of radioelements between solutions and the crystalline precipitates of some salts served as an indication of the presence of true isomorphism between the corresponding compounds of the microcomponent and the substance of the solid phase and so to the correspondence of their chemical composition and structure.

In further studies this theory permitted demonstration of the presence of a series of molecular compounds of radon and initiated the study of chemical compounds of the noble gases which was carried on by Nikitin. Work on distribution was extended to the field of fusions. Studies were made of the distribution of radioelements between two immiscible solvents (B. A. Nikitin and others).

In connection with the use of atomic energy for peaceful purposes, Soviet chemists were forced to devote particularly serious attention to the development of extraction and sorption methods for the separation of radioelements of industrial value. In this field they studied in detail the mechanism of removing radioactive isotopes from aqueous solution by organic solvents (Vdovenko and co-workers).

Many studies were made of the adsorption of radioelements (Khlopin, Nikitin, Ratner, I. E. Starik, Nikolsky, and others). This work on distribution and adsorption made it easier to separate and purify radioelements in industrial processes.

The separation of uranium and thorium was studied over a wide range of thorium concentrations and a chromatographic purification was developed for removing microquantities of zirconium and niobium: a method was found for studying complex formation in solution by simultaneous adsorption of the central ion by anionite and cationite (Nikolsky and students). The choice of adsorbents for some radioelements on ion-exchange resins, silica gel, and other porous adsorbents was studied (Nikolsky, D. N. Starzhesko). As a result of the study of the adsorption of polonium and its colloidal properties, the actual existence of a true colloidal radioelement was shown (Starik). Work was carried on upon the use of natural radioelements as indicators in analytical chemistry (Vict. I. Spitsyn, Starik).

The use of artificial radioelements as indicators was begun even in the thirties, for studies of many fundamental questions such as the nature of the chemical bond, isotopic exchange between solid phase and solution, structure of complex structure of complex compounds, and kinetics and mechanism of catalytic reactions (Grinberg, Polesitsky, Roginsky). Later, the method of labeling atoms was used in many different fields of chemistry (Brodsky, An. N. Nesmeyanov, Alimarin, Spitsyn, Fialkov, Syrkin, D. N. Kursanov, Razuvaev, and others).

In the post-war period, the chemistry of nuclear transformations and of the transuranium elements has been intensively developed. (A. P. Vinogradov, B. V. Kurchatov, Nikitin, Alimarin, A. N. Murin). A method was worked out for separating radioactive isotopes of a number of elements by irradiation of their organic compounds (Murin, V. D. Nefedov, and others).

Shchukarev first presented the idea of periodicity in the atomic nucleus (1923) and formulated the rule for the stability of isobars which explained the occurrence, in the middle of the system, of elements which did not have stable isotopes.

At the present time, as we know, fission is the nucleus and the periodicity from it which generates the well-known anomalies of atomic weight and other nuclear peculiarities is recognized by science to be due to the isobar rule which explains the instability of technetium and promethium.

The fundamental studies of Butlerov in organic chemistry which established the theory of chemical structure were carried out in the 1860's and 1870's. Great progress in the development of Butlerov's structural theory came from the work of his famous students, V. V. Markovnikov, A. M. Zaitsev, B. B. Vagner, M. I. Konovalov, and others.

Beginning at the end of the last century and during the first half of the present one, two schools of Soviet Russian chemistry swiftly developed, the very strong and numerous school of Zelinsky and the large school of Favorsky. Developing the well known works of Zinin, Butlerov, Markovnikov, Zaitsev, Vagner, Konovalov, Zelinsky, and Favorsky, Soviet organic chemists in the last forty years have made great and important contributions to organic chemistry. Particular interest was shown in the study of the simplest organic molecules, their synthesis, stability, and reactions, etc. Studies in this field had a clear purpose – deep understanding and search for the chief general laws which determine the structure, reactivity, and mechanism of the many transformations of the basic types of organic compounds (Zelinsky, Favorsky, A. E. Chichibabin, N. Ya. Demyanov, S. S. Nametkin, A. E. Arbuzov, A. N. Nesmeyanov, P. P. Shorygin, A. E. Porai-Koshits, S. V. Lebedev, B. A. Kazansky, V. M. Rodionov, and their school). Such basic and general phenomena of organic chemistry included isomerism and isomeric transformations, tautomerism and tautomeric transformations, intramolecular rearrangements, polymerization and condensation, splitting of organic molecules to form free radicals, stability and instability of cyclic and bicyclic compounds, questions of stereochemistry, strength of chemical bonds, reaction mechanisms, etc. Soviet organic chemists conducted many original investigations in these fields, opening up new questions and problems and discovering broad prospects for further scientific research. Such work characterizes the high level of Soviet organic chemistry.

Important theoretical and experimental studies have been made in recent years on reaction mechanisms and the reactivity of organic compounds. These studies, conducted in the light of modern ideas of physics and chemistry, have greatly developed organic chemistry (A. N. Nesmeyanov, A. I. Kiprianov, D. N. Kursanov, E. A. Shilov, M. M. Shemyakin, M. I. Kabachnik, O. A. Reutov, and others).

Studies by Soviet organic chemists have provided new and original methods of synthesis of different classes of organic compounds, and methods for isolation of a number of valuable products from natural sources.

Zalinsky and Favorsky and their students have devoted much attention to the study of hydrocarbons. With imagination and strict logic, the systematic studies of Zelinsky and the members of his school have covered different fields of chemistry for more than seventy years. Among the most basic studies of Zelinsky were the investigations on hydrocarbons.

The scientific activities of Zelinsky were successful and productive in the pre-revolutionary period, but their scope, character, and tempo did not compare with those of the Soviet period. Besides his extremely important scientific activities, Zelinsky achieved great success in training highly qualified workers in the field of chemistry.

In the field of organic synthesis, Zelinsky and his students obtained scores of hydrocarbons of different classes. The contact transformation of acetylene into benzene had great theoretical and practical importance (Zelinsky, Kazansky). New and original methods of synthesis were worked out for unsaturated hydrocarbons, permitting strict determination of the position of the double bonds in the molecule, and also a new synthetic method for homologs of cyclopropane (R. Ya. Levina and co-workers). A new process was developed for obtaining the diethyl ester of cyclobutan-1, 1-dicarboxylic acid (Kazansky, V. P. Golmov) – a starting compound for the synthesis of cyclobutane hydrocarbons. Many cyclobutane and cyclopropane hydrocarbons were synthesized (Zelinsky, Kazansky, and students).

As a result of the many investigations of the Zelinsky school a large number of compounds were obtained: mono-, bi-, and tricyclic hydrocarbons, spiranes, and muti-ring compounds, many of which had great theoretical and practical interest.

The work of the Zelinsky school showed that two classes of hydrocarbons – the aromatic and the hexahydroaromatic – could be interconverted under certain conditions of catalysis and temperature. This work revealed the wide possibilities of studying the nature of petroleum, its properties, composition, and treatment.

Many investigations were made in the field of hydrogenation and dehydrogenation catalysts. These included detailed studies of the dehydrogenation of cyclic into aromatic hydrocarbons under the catalytic influence of platinum or palladium deposited on activated carbon, or of nickel deposited on aluminum oxide. It was shown that dehydrogenation of cyclohexane, its homologs, and decahydronaphthalene went to completion under the proper conditions (Zelinsky, N. I. Shuikin, Yu. K. Yuryev, and others). Catalytic dehydrogenation of cyclohexane hydrocarbons also occurred when they were mixed with hydrocarbons of other classes, which remained unchanged. This discovery of "selective catalytic dehydrogenation" was used for the study of petroleum from different regions and a method based on it was developed for investigating the composition of benzine (Zelinsky, Kazansky, Shuikin, Yuryev, and others). This method had great theoretical and industrial value. (Zelinsky, Shuikin). It was shown that the catalytic dehydrogenation of polynuclear polymethylene hydrocarbons was accompanied by secondary effects. Thus, dicyclohexylmethane was converted into flucrene, dicyclohexylethane into phenanthrene (Zelinsky, I. N. Tits, and others). The bicyclic hydrocarbons carane, pinane, thujane, and methylethylenecyclohexane were transformed with rupture of a bridge into the corresponding aromatic hydrocarbons, cymene, benzene, toluene; cyclofenchene was converted into a mixture of fenchenes: fenchane, isobornylane (Zelinsky, Levina, Kazansky, A. F. Plate, and others).

Incompletely hydrogenated aromatic hydrocarbons in the presence of the same catalyst but at lower temperatures were converted into aromatic hydrocarbons and saturated cycloparaffins (for example, cyclohexene into cyclohexane and benzene). This effect was called "irreversible catalysis" (Zelinsky). It was also shown that cyclic hydrocarbons with double and triple bonds in the side chain could undergo irreversible catalytic changes (Zelinsky, Kazansky, Levina). On further study of the hydrogenation of cyclopentane hydrocarbons in the presence of platinized carbon, it was found that if the side chain of the cyclopentane hydrocarbon held four or more carbon atoms, aromatic hydrocarbons were formed on hydrogenation (Kazansky, Plate).

Discovery of the mechanism of formation of aromatic hydrocarbons by closure of new six-membered rings from the side chain led to the idea of the possibility of direct transformation of paraffin hydrocarbons into aromatics. These reactions of catalytic aromatization, consisting in the formation of new six-membered rings from aliphatic side chains (Zelinsky, Kazansky, Plate, B. L. Moldavsky, V. I. Karzhev, and others), opened wide prospects for obtaining aromatics from aliphatic raw materials Since they presented problems of great theoretical and practical interest, reactions of aromatization of paraffins were submitted to detailed study (Zelinsky, Kazansky, Plate, P. P. Bornsov, A. L. Liberman, M. S. Eventova, E. M. Tarasova, S. I. Khromov, S. R. Sergienko, I. B. Losik, and others).

It was shown that cyclopentane at 310° in the presence of platinized carbon and hydrogen underwent splitting of the five-membered ring with smooth transformation into n-pentane (Zelinsky, Kazansky, Plate). These reactions were general for all homologs of cyclopentane; for example, 1,2,3-trimethylcyclopentane was converted into 2,3,4-trimethylpentane (M. I. Batuev, Kazansky, A. V. Koperina), hydrindane was converter into o-ethyltoluene (M. B. Turova-Polyak), α-naphthylcyclopentane formed a mixture of α-amylnaphthyl and peri-trimethylenenaphthalene (Khromov), etc.

It was shown that the simplest homologs of cyclopropane and cyclobutane underwent rupture of the ring more easily than homologs of cyclopentane (Kazansky, V. A. Lukina, V. A. Ovodova). Later it was found that in the presence of a platinum catalyst, paraffin hydrocarbons could be cyclized not only to form six-membered rings but also to form cyclopentane hydrocarbons (Kazansky, Liberman). Thus, n-heptane gave trans-1,2-dimethylcyclopentane, etc.

Catalytic hydrogenation methods were worked out in detail, using platinized or palladized carbon, and osmium for hydrogenation of unsaturated and aromatic hydrocarbons. Thus in the hydrogenation of o-xylene in the presence of ozmium even at 50-60° cis-1,2-dimethylcyclohexane was preferentially formed, and on hydrogenation of the same hydrocarbon in the presence of platinum trans-1,2-dimethylcyclohexane was preferentially formed (Zelinsky, E. I. Margolis).

Many studies by Zelinsky cast light on isomeric transformations of cyclic hydrocarbons under the influence of anhydrous aluminum chloride or bromide. He showed that in the presence of these catalysts there occurred

easy conversion of cis-decalin into trans-decalin, and of cis-hydrindane into trans-hydrindane (Zelinsky, Turova-Polyak); homologs of cyclopentane were converted at temperatures not above 100° into homologs of cyclohexane, and at higher temperatures the reverse transformation occurred.

It was established that cyclohexene in the presence of aluminum oxide, silica gel, and beryllium oxide at 400-450° was completely converted to methylcyclopentene (Zelinsky, Yu. A. Arbuzov).

Many investigators of the Zelinsky school showed that, depending on conditions of isomerization, all polymethylene rings could be interconverted. They studied transformations of hydrocarbons of the paraffin series. 3,7-Dimethyl-1-octene passed over platinized asbestos at 200° completely isomerized with a shift of the double bond to form 3,7-dimethyl-2-octene (Zelinsky, Levina).

In later years they studied many cases of isomeric transformations in different classes of hydrocarbons (Levina and co-workers). Many investigations were made on alkylation of hydrocarbons (Zelinsky, Shuikin, Turova-Polyak, and others); dealkylation of cyclopentane, cyclohexane, and benzene homologs (Zelinsky, Khromov, S. S. Novikov, and others); on pyrolysis of petroleum products (Zelinsky, B. M. Mikhailov, Yu. A. Arbuzov), cyclopentane and methylcyclopentane (Kazansky, Plate); on oxidation of hydrocarbons (Borisov, Eventova, A. N. Titova). A new theory of catalysis was developed (Zelinsky), which has now been successfully expanded by students of Zelinsky (Balandin). The structure of proteins was studied (Zelinsky, N. I. Gavrilov, and others).

There have been many syntheses of different hydrocarbons for use as motor fuels, higher aliphatic and cyclic hydrocarbons (A. D. Petrov).

Important results were obtained in studying the properties and composition of petroleum, in treating and purifying its distillates, and in developing new methods for desulfuring oil products (Nametkin). Many studies were made on cracking processes and the pyrolysis of petroleum (A. F. Dobryansky, A. V. Frost, Nametkin, and others).

Studies were made on the alkylation of phenols by alcohols in the presence of aluminum chloride, phosphoric acid, anhydrous ferric chloride and zinc chloride and of polyhalobenzenes in the presence of metallic aluminum, and of cyanoethylation of the aromatic nucleus. There were studies of the condensation of alcohols, vinyl ethers, allylacetate, styrene and other compounds with aromatic hydrocarbons in the presence of aluminum chloride (I.P. Tsukervanik).

A second type of camphene rearrangement, the "Nametkin rearrangement," was found, which permitted the transfer of the camphor group from homologs of camphor to other compounds and the study of the mechanism of intramolecular rearrangements (Nametkin). Studies were made on the chemical composition and structure of terpenes, the isomeric conversion of terpene hydrocarbons and terpene oxides, and the isomerization of bicyclic terpenes into terpenes with a straight chain (B. A. Arbuzov). A method was worked out for obtaining camphor from turpentine by a process of isomerization of α-pinene into camphene (V. E. Tishchenko, G. A. Rudakov). The chemistry of resin acids was studied (V. N. Krestinsky, B. A. Arbuzov); the diene synthesis was used to establish the position of the conjugated double bonds in the resin acid molecule (B. A. Arbuzov). Studies were made of the synthesis of terpene oxides and oxides of unsaturated fatty acids isolated from the ethereal oils of plants (G. V. Pigulevsky and co-workers). A path was discovered for passing from acetylene hydrocarbons to terpenes and a scheme for the formation of terpenes in nature was proposed (Favorsky).

On the basis of many studies of the formation and transformations of ethereal oils and resins in conifers, a hypothesis was proposed for the formation in plants of esters which split under enzyme action into hydrocarbons and resin acids by a type of decomposition like that of tertiary alcohols (Pigulevsky).

Soviet chemists have made many studies in the field of heterocyclic compounds. They have completed investigations of catalytic hydrogenation and dehydrogenation of pyridine and piperidine in the presence of metallic palladium (Zelinsky, P. P. Borisov). As a result of much work by the Zelinsky school in the field of catalytic transformations of heterocycles a new pathway of reciprocal transformations was found which connected different groups of heterocyclic compounds that had earlier been considered independent and unrelated (Zelinsky, Borisov, Yuryev, Shuikin, G. S. Pavlov, M. I. Ushakov, and others). They studied the contact conversions of five-membered heterocyclic compounds – furan, pyrrole, and thiophine (Yuryev and co-workers). A method of sulfonating acidophobic compounds was worked out, opening a new class of compounds – the sulfoacids of diene hydrocarbons, quinones, furan compounds, pyrroles, indoles, etc. (A. P. Terentyev). Studies

were made of pyridine compounds; the synthesis was worked out for the pyridine analog of Michler's ketone and hydrol, and for dyes of the triphenylmethane type (I. L. Knunyants).

The chemistry of the aryl amides of hydroxycarboxylic acids and their conversion to heterocyclic compounds was investigated (P. A. Petyunin). The chemistry of 1,3-indandione and its derivatives was studied (G. Ya. Vanag). Heterocyclic compounds were obtained from hydrazide (1,3,4-triazol-5-thione), and the hydrolysis of some heterocyclic sulfones was studied (I. Ya. Postovsky). Benzimidazoles were examined, and pyrazolones were synthesized from diketene (B. A. Porai-Koshits). Derivatives of acetoacetic acid and pyrimidines were prepared and the characteristic behavior of the methyl group in heterocycles was studied (N. V. Khromov-Borisov). Diketene reactions were examined (V. V. Perekalin).

Reactions were discovered for enlarging carbocyclic rings and those containing oxygen, nitrogen, or sulfur (Demyanov). The amination and hydroxylation of pyridine was investigated (Chichibabin). Many studies were made of amino acids and their derivatives (V. M. Rodionov, V. V. Feofilaktov). Simple and accessible paths were discovered for obtaining β-amino acids by condensation of aliphatic, aromatic, and heterocyclic aldehydes with maleic acid in the presence of solutions of ammonia (Rodionov). A new method was worked out for obtaining γ-acetopropyl alcohol (Knunyants) which is widely used in producing vitamin B_1 and antimalarial preparations such as quinovin.

Wide and original studies were made of the synthesis and structure of antibiotics, withpreparation of synthomycetin and levomycetin, the best drugs against typhus, trachoma, and dysentery (Shemyakin and coworkers).

Much progress was made in the field of the alkaloids. The study and basic production of morphine was carried out for the first time in the USSR and a new process was discovered for obtaining codeine by methylation of morphine (Rodionov). Much systematic work was done on the analysis of plants which contained alkaloids such as anabasine, which is widely used in the fight against plant pests (A. P. Orekhov); much light was thrown on alkaloid structure, and methods for classifying alkaloids on the basis of their structures (Orekhov, P. A. Konovalova).

Anabasine was investigated (B. Kh. Timbekov, A. S. Sadykov), and alkaloids from different plants were studied (S. Yu. Yunusov, Kh. A. Aslanov, and others). The synthesis of pilocarpine was completed (N. A. Preobrazhensky). The structures of the alkaloids heleotrine, lazeocarpine, and trichodesmine were cleared up (G. P. Menshikov). Many derivatives of acridine and sulfamide compounds were prepared and studied (O. Yu. Magidson), as were derivatives of quinuclidine (M. V. Rubtsov), uses were tested for β-sitosterol (along with cholesterol) in the synthesis of steroid hormones, and the structure of benz-2, 1,3-thiothiazole and its derivatives were examined (A. M. Khaletsky). Much work was done on the synthesis and isolation of vitamins from plants, the determination of their composition and structure, and their practical use.

A. E. Favorsky and his students made most of their studies on acetylene hydrocarbons and their derivatives. They investigated general phenomena such as the acetylene-allene-diene isomerizations (T. A. Favorsky, A. I. Zakharova), isomerization and polymerization of unsaturated hydrocarbons, intramolecular rearrangements, etc. They worked out a method for preparing acetylene alcohols by condensation of acetylene with different ketones in the presence of solid potassium hydroxide (Favorsky). All these studies led to various methods for obtaining synthetic rubber, especially isopropene (Favorsky) and chlororubbers (A. L. Klebansky). They studied electrolytic hydrogenation of acetylene alcohols and glycols, especially dimethylethynyl carbinol to dimethylvinyl carbinol,which by hydrogenation is transformed into linalool, geraniol, and terpene hydrate (Favorsky, A. I. Lebedeva).

The work of Favorsky and his school solved the problem of getting synthetic rubber in the USSR. In the thirties S. V. Lebedev worked out an industrial process for manufacturing it. Lebedev made extensive studies of the chemistry of diene hydrocarbons, the polymerization of ethylene and diene hydrocarbons, and depolymerization processes. In developing the classical work of Lebedev, investigations were continued on the relation between methods of making synthetic rubber, its structure, and its properties (A. I. Yakubchik, Klebansky, Yu. A. Gorin, and others). The isomerizations of allene and diene hydrocarbons into three and four-membered substituted rings were investigated (Ya. M. Slobodin).

Numerous studies were made on combining reactions, condensations,etc.of compounds with joining of multiple bonds (A. A. Petrov and co-workers). Polymerizations of a number of diene compounds were examined in detail (B. A. Dolgoplosk, B. A. Dogadkin, S. S. Medvedev). The diene synthesis was successfully used for obtaining

many complex organic substances and studying the structure of diene compounds (B. A. Arbuzov, I. N. Nazarov, A. A. Petrov, and others).

Numerous new acetylene derivatives were synthesized. Vinylethyl carbinols were obtained and studied and the chemistry of unsaturated ketones was worked out, including their transformation into heterocyclic and five-membered rings (Nazarov and co-workers). As a result of studies of the diene synthesis, steroids were obtained which were sources of androgens, original work was done on the mechanism of cyclization, the diene synthesis, polyene rearrangements, and the stereochemistry of cyclic and heterocyclic compounds (Nazarov and co-workers). Wide use was found for the carbinol adhesives obtained by Nazarov and for the anesthetic promedol.

In developing the work of Favorsky on the arrangement of multiple bonds in rings, the question of the possible existence of allene and acetylene bonds in cyclic hydrocarbons was studied (N. A. Domnin). Much original work was carried out on the chlorination of different aliphatic, cyclic, and terpene hydrocarbons (D. V. Tishchenko and co-workers). The activity of the halogens in relation to their position in the molecule was considered (B. V. Tronov and co-workers). On the basis of the Favorsky reactions, industrial methods were developed for obtaining simple vinyl ethers and acetaldehyde from acetylene and alcohols in the presence of potassium hydroxide (M. F. Shostakovsky).

In developing the classical work of Favorsky on oxygen-containing compounds, his students made great contributions to the chemistry of carbonyl and hydroxycarbonyl compounds. They made detailed studies of simultaneous intramolecular oxidation— reduction reactions, the transformations of hydroxyaldehydes and hydroxyketones, isomerizations of ketoalcohols, aldehydes, and hydroxyaldehydes (S. N. Danilov, E. D. Venus-Danilova). These studies supplied an explanation for the oxidation-reduction reactions of the sugars during alcoholic fermentation and other reactions (Danilov). The isomerization of tertiary α-ketoalcohols was studied (Khaletsky).

In further studies the tautomeric α-ketoalcohols were fixed as methyl ethers and the transformations of these compounds were studied (T. I. Temnikova). A series of interesting and important studies were carried out on the reactions of aliphatic diazo compounds (I. A. Dyankonov).

A process for catalytic hydrogenation of acetylene alcohols was developed, and the question of the connection between hydrogenation, chemical nature of the catalyst, and structure of the hydrogenated compound was considered (Yu. S. Zalkind).

Studies were made of the rate and mechanism of oxidation of aliphatic and aromatic hydrocarbons, alcohols, esters, amines, amino acids, and other compounds by different oxidizing agents (Tronov and co-workers).

A catalytic method was developed for the synthesis of complex ethers from primary alcohols, with investigations of the processes of condensation, dehydration, and cyclization (B. N. Dolgov). Original studies were made on the synthesis and isomerization of simple carboxyl compounds, and the reactions of oxides of nitrogen with unsaturated compounds were investigated, resulting in a process for obtaining diamines and hydroxyamines (Demyanov). The classical synthesis of cyclopropene and vinylcyclopropane was accomplished (Demyanov and others). Studies were made of reactions of nitration (A. V. Titov), halogenation, polymerization, and alkylation of different classes of hydrocarbons (A. V. Topchiev, Tronov and co-workers).

In the Soviet period there has been rapid development of dye chemistry (M. A. Ilyinsky, N. M. Kizhner, A. E. Porai-Koshits, Rodionov, N. N. Vorozhtsov Senior, Kiprianov, and others). Many methods for obtaining different organic dyes and intermediates were developed. Success was attained in studying the mechanism and theory of the sulfonation reaction and of alkaline fusion (A. B. Porai-Koshits, Vorozhtsov, Sr., and others), of arylization and alkylation of amines and phenols, of diazotization and combination with nitrogen (Rodionov) and of the chemistry of indigo dyes. Valuable studies were made on the chemistry of anthracene and its derivatives (Ilyinsky). A chemical theory of dyeing was developed (Porai-Koshits) and the effect of different substituents of the reactivity and the color of different dyes was examined. Work was carried out on the connection between color and molecular structure (V. A. Izmailsky, Kiprianov, and others).

A series of studies cast light on the chemistry of hydroxyfuchsin dyes (I. S. Ioffe) and the structure and reactions of diazo compounds (E. V. Grachev, B. A. Porai-Koshits). Valuable work was done on the synthesis of carbocyanide dyes with practical importance (Knunyants).

In recent years the scientific investigation of high molecular weight compounds has attained especially important theoretical and practical value, since proteins, plastics, rubber, cellulose, synthetic fibers, etc. belong to this class. Physical methods have been widely used in these studies and have given detailed information of the composition, structure, and properties of large molecules. Extensive studies have been made for the purpose of obtaining plastics with individual properties. Investigations were made of the polymerization of vinyl chloride, vinyl acetate (S. N. Ushakov), phenol-formaldehyde resins, amino plastics (A. A. Vansheidt, G. S. Petrov), and of polymers of styrene and its homologs (Shorygin). Different methods were worked out for getting plastics. Studies were made of the chemistry of nitrocellulose, cellulose ethers and esters, and viscose (Shorygin, N. I. Nikitin, Danilov, Ushakov, Z. A. Rogovin).

The laws, conditions and mechanisms of polymerization and polycondensation were worked out for different organic compounds (V. V. Kirshak, Medvedev, M. M. Koton, and others). These studies were designed to solve questions of great theoretical importance, so that the results could be used in practice (the manufacture of high quality synthetic fibers, plastics, and films).

In the course of many years the chemistry of organic compounds containing other elements has been studied. Especially numerous were the investigations of organophosphorus compounds, their synthesis, structure, and properties (A. E. Arbuzov, B. A. Arbuzov, and A. V. Kirsanov with their students). They perfected the synthesis homologs of phosphoacetic acid and studied new methods for obtaining free radicals of the trimethymethylene series, methods of preparing esters of hypophosphoric, pyrophosphoric, and pyrophosphorous acids and their derivatives, and compounds with asymmetric phosphorus atoms, and they worked out the reactions of esters of phosphorus acid with unsaturated compounds. Many detailed studies were made of the tautomerism of organophosphorus compounds (A. E. Arbuzov, B. A. Arbuzov). Systematic investigations gave new methods for the synthesis of esters of phosphorous and thiophosphorous acids, and for the study of the anomalous reactions of α-haloketones with phosphorites (A. N. Pudovik and co-workers). Organoarsenic compounds were successfully studied especially for the production of asymmetric compounds of arsenic (G. Kh. Kamai and co-workers).

Synthetic methods using organosodium compounds (Shorygin), and organolithium compounds (K. A. Kocheshkov) were worked out, and substitution of hydrogen by sodium in aromatic compounds was discovered (Shorygin). The chemistry of magnesium organic compounds and the mechanism of the Zaitsev-Grignard reaction were studied (Terentyev and others).

The organomagnesium synthesis was widely used for preparing hydrocarbons (A. D. Petrov), alcohols (Nazarov), acids and amines (Kocheshkov) and for studying free radicals (Razuvaev). Particularly in recent years the chemistry of organosilicon compounds has been developed (A. D. Petrov, B. N. Dolgov, and others). Methods have been found for obtaining highly polymerized organosilicons for plastics, lacquers, dielectrics, etc. (K. A. Andrianov and co-workers). The synthesis and physicochemical properties of new classes of organosilicon compounds were studied (Topchiev and co-workers). The chemistry of fluoro-organic compounds was investigated (Knunyants) and many new compounds of this type were obtained.

Very wide and interesting theoretical advances were made in the chemistry of metalloorganic compounds with the heavy metals. A great contribution of the general development of theoretical organic chemistry resulted from this work (A. N. Nesmeyanov and his school). Nesmeyanov discovered and developed the diazo method for the synthesis of aromatic mercury compounds. This method was extended to the synthesis of metalloorganic compounds of tin, lead, thallium, antimony, bismuth, magnesium, zinc, cadmium, aluminum, and arsenic. The general method for introducing mercury permitted conversion of any metalloorganic compound to a mercury derivative. Detailed studies were made of the mechanism of formation of mercury organic compounds through diazo compounds, the mechanism of adding metal salts to unsaturated compounds and of the structure of such addition products (Nesmeyanov, R. Kh. Friedlin, and others).

Studies were conducted on the chemistry of quasi-complex metalloorganic compounds, the effects of tautomerism, the decomposition of various diazonium and iodonium compounds, the causes and mechanism of the transfer of reactive centers, the laws controlling the nonformation of some stereochemical configurations in electrophilic processes, and of radical substitution on a carbon atom at a double bond (Nesmeyanov and his school).

The subjects discussed above are only some of the trends and results in the development of chemistry and make up only part of the scientific work during the years of Soviet rule. In this survey we have briefly noted the principal works on general and theoretical questions which have appeared in the Journal of General Chemistry; but even in this sense we have not been able to mention a large number of important works by Soviet chemists, although they also are of general value and great theoretical interest. We assume, however, that those papers which we have not mentioned will be evaluated in other Soviet journals whose number has greatly increased during the Soviet period.

During these years chemistry in the USSR has developed rapidly and the rate of its progress has increased every year. We can judge the scale and speed of development of scientific research in the USSR by the growth of the chemical literature. In the 40 years a great number of original and translated books on chemistry have appeared: monographs, textbooks, survey papers, collections of the works of famous chemists, etc. A whole series of new journals were published such as the Journal of Physical Chemistry, Journal of Inorganic Chemistry, Journal of Analytical Chemistry, Colloid Journal, Journal of Applied Chemistry, Progress of Chemistry, Bulletin of the Academy of Sciences of the USSR Division of Chemical Science, Chemical Science and Industry, Ukrainian Chemical Journal, Chemical Industry, Factory Laboratory, Abstract Journal (Chemistry), and many Reports, Bulletins, and Proceedings of scientific research and teaching institutions. Each year hundreds of scientific papers by Soviet chemists appear in these journals. Each year also the number of papers increases in the oldest chemical journal (founded by Mendeleev and Butlerov), The Journal of General Chemistry.

From its modest beginning in 1869, The Journal of the Russian Chemical Society, now the Journal of General Chemistry, has grown and expanded in the Soviet period in spite of the appearance of many other chemical journals. Thus, in 1918 the journal had 670 pages, in 1928, 1800, in 1930, 2358, and in 1956, 3515 pages.

Even in the first years of the Soviet government, new scientific research institutes and laboratories for chemistry were founded, such as the Central Chemical Laboratory of the VSNKh, from which arose the L. Ya. Karpov Physicochemical Institute, the Institute of Platinum and Other Precious Metals, now the Institute of General and Inorganic Chemistry of the Academy of Sciences, the Institutes of Physicochemical Analysis, of Chemical Physics, of Applied Chemistry, of Physical Chemistry, of Organic Chemistry, of Rare Elements, and many others.

In many higher schools and institutions for scientific research under the Soviet Government hundreds and thousands of highly skilled workers have been trained as chemists both for scientific research and for the numerous fields of chemical industry.

Soviet chemistry has formed firm bonds with chemical industry and Soviet technology.

The demands of the rapidly developing socialist industry call for deep and extensive study of processes of combustion, explosions, catalysis, etc. The scientific basis for an understanding of these processes and phenomena depend upon the theoretical work of Soviet scientists, Semenov, Balandin, Roginsky, Kobozev, and their school. In the electrochemical industry the work of Frumkin, Izgaryshev, P. P. Fedotyev, Izbekov, S. V. Karpachev, and others is widely used. The chemistry of metallic alloys, aqueous salt solutions, fused salts, silicates, table salt manufacture, etc. has been based on the work of Kuranakov and his school.

The work of Zelinsky and his school has opened wide possibilities for the study of petroleum, its composition, properties, and industrial treatment. It has made possible catalytic cracking, destructive hydrogenation, polymerization of cracking gases, etc.

The work of Favorsky and his school has opened the possibility of industrial production of technically valuable products – the solvent dioxane, vinyl ethers and acetaldehyde, adhesives and anesthetics, high molecular weight compounds, and especially synthetic rubber.

The history of the development of chemical science and industry and their theoretical and practical experiments clearly shows that theoretical work in chemistry always serves as an essential base for industry. The essential base for the development of theoretical chemistry and industry is in part the work published in the Journal of General Chemistry.

Under the capitalistic regime in Russia this base remained hidden, dead and fruitless. Only the October Revolution and the Soviet regime made the theoretical work of Russian chemists a starting point for further development of Soviet chemical science and socialistic industry.

Only since the October Revolution have Soviet chemists, like all Soviet scholars, become active as creators and builders of communist society; they along with the whole Soviet nation gladly celebrate the 40th anniversary of the Soviet regime and face with enthusiasm the struggle for new successes in the building of communism.

LITERATURE CITED

[1] N. V. Ageev, "Nature of solid metallic phases of variable composition," Progr. Chem. 21, 1058 (1952).

[2] V. Ya. Anosov, and S. A. Pogodin, Basic Beginnings of Physicochemical Analysis* (Acad. Sci. USSR Press, 1947).

[3] K. A. Andrianov, "The mechanism of formation and reactions of organosilicon polymers," Progr. Chem. 24, 430.

[4] A. E. Arbuzov, Short Sketch of the Development of Organic Chemistry in Russia* (1948).

[5] A. E. Arbuzov, "Organic derivatives of the acids of phosphorus," Progr. Chem. 20, 521 (1951).

[6] A. A. Balandin, B. M. Berkengeim and A. N. Nesmeyanov "Soviet chemistry and the thirtieth anniversary of the October Revolution," Progr. Chem. 16, 513 (1947).

[7] A. I. Brodsky, The Chemistry of Isotopes* (Acad. Sci. USSR Press, 1952).

[8] Questions of Chemical Kinetics, Catalysis, and Reactivity,* (Acad. Sci. USSR Press, 1955).

[9] S. N. Danilov, Molecular Rearrangements and Intramolecular Oxidation-Reduction Reactions; Reactions and Methods of Study of Organic Compounds,* Book 4, (State Sci.-Tech. Press for Chem. Lit., 1956).

[10] S. N. Danilov, Sketch of the Scientific Activities of Academician A. E. Favorsky* (Collected Works of A. E. Favorsky) (Acad. Sci. USSR Press, 1940).

[11] 220 Years of the Academy of Sciences of the USSR, Chemical Science* (Acad. Sci. USSR Press, 1945).

[12] N. Ya. Demyanov, Collection of Published Works* (Acad. Sci. USSR Press, 1936).

[13] N. A. Domnin, "In memory of A. E. Favorsky (Scientific Activities)," J. Gen. Chem. 16, 1317 (1946).

[14] M. M. Dubinin, "Adsorption of Gases and Vapors and the Structure of the Adsorbent," Progr. Chem. 21, 513 (1952).

[15] I. I. Zhukov, Sketch of the History of Chemistry in the St. Petersburg – Leningrad – University for 125 Years. Proceedings of the Jubilee Session, Div. Chem. Sci. (Leningrad University Press, 1944).

[16] N. D. Zelinsky, Collected Works* (Acad. Sci. USSR Press, 1941).

[17] M. I. Kabachnik, "Some problems of tautomerism," Progr. Chem. 25, 137 (1956).

[18] A. I. Kitaigorodsky, Organic Crystal Chemistry* (Acad. Sci. USSR Press, 1955).

[19] N. I. Kobozev, "The physical and mathematical basis for the theory of active centers," Progr. Chem. 25, 545 (1956).

[20] V. N. Kondratyev, and N. M. Emanuel, "Valuable reactions and processes of combustion and explosion," Progr. Chem. 25, 393 (1956).

[21] V. V. Korshak, "Basic laws of polycondensation," Progr. Chem. 21, 121 (1952).

[22] M. M. Koton, "Progress in the Field of Obtaining New Polymers," Progr. Chem. 24, 901 (1955).

[23] S. V. Lebedev, Life and Works* (ONTI, Khimteoret, 1938).

[24] P. G. Maslov, "Oscillations of the molecule and the thermodynamic properties of organic compounds," Progr. Chem. 25, 1069 (1956).

[25] I. N. Nazarov, "Progress of organic syntheses based on acetylene," Progr. Chem. 20, 309 (1951).

[26] I. N. Nazarov, and L. D. Bergelson, "Stereochemistry of steroid compounds," Progr. Chem. 21, 5, 566 (1952).

* In Russian.

[27] S. S. Nametkin, (Collected Works)* (Acad. Sci. USSR Press, 1954).

[28] A. N. Nesmeyanov, "Conjugated Bonds," Sci. Repts., Moscow State University, No. 132, Organic Chemistry, Book 7, 5 (1950).

[29] A. N. Nesmeyanov "Characteristic Features of the Development of Organic Chemistry in the USSR in 25 Years," Progr. Chem. 12, 18 (1943).

[30] A. N. Nesmeyanov and M. I. Kabachnik, "Duplication of reactivity and tautomerism," J. Gen. Chem. 25, 41 (1955).**

[31] A. N. Nesmeyanov, B. A. Kazansky, A. F. Plate, O. A. Reutov, N. K. Kochetkov, A. A. Balandin, R. Ya. Levina and Yu. K. Yuryev, Review Papers, Sci. Repts., Moscow State University, No. 175, Organic Chemistry (1956).

[32] A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, "Study of the chemical reactions of polychlorohydrocarbons," Progr. Chem. 25, 665 (1956).

[33] A. A. Petrov, "New progress in the field of the chemistry of 1,3-diene halogen compounds," Progr. Chem. 13, 203 (1944).

[34] A. A. Petrov, "Progress in the field of divinyl chemistry," Progr. Chem. 22, 905 (1953).

[35] A. F. Plate, Catalytic Aromatization of Aliphatic Hydrocarbons* (Acad. Sci. USSR Press, 1948).

[36] Problems of the Mechanism of Organic Reactions, Reports of the Kiev Session of June 2-5, 1952 (Acad. Sci. USSR Press, 1953).

[37] O. A. Reutov, "Homolytic reactions in the chemistry of heteroorganic compounds," Progr. Chem. 23, 426 (1954).

[38] O. A. Reutov, Theoretical Problems of Organic Chemistry,* (Moscow University Press, 1956).

[39] S. Z. Roginsky, The Theoretical Basis for the Isotope Method of Studying Chemical Reactions* (Acad. Sci. USSR Press, 1951).

[40] N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity* (Acad. Sci. USSR Press, 1954).

[41] Soviet Chemistry in Twenty-five Years (Collection of Papers),* (Acad. Sci. USSR Press, 1944).

[42] The State of the Theory of Chemical Structure in Organic Chemistry, Div. Chem. Sci. Acad. Sci. USSR* (Acad. Sci. USSR Press, 1954).

[43] Report of the All-Union Session on Catalysis (Acad. Sci. USSR Press, 1950).

[44] A. E. Favorsky, Collected Works* (Acad. Sci. USSR Press, 1940).

[45] N. A. Figurovsky, G. V. Bykov and T. A. Komarova, Chemistry in Moscow University for 200 Years* (Moscow University Press, 1955).

[46] A. A. Frumkin and others, Kinetics of the Electrode Process* (Moscow University Press, 1952).

[47] Electrokinetic Properties of Capillary Systems – Monograph, edited by P. A. Rebinder* (Acad. Sci. USSR Press, 1956).

[48] Jubilee Papers Collected for the 30th Anniversary of the October Revolution, Part 1, pp. 473-709 (Acad. Sci. USSR Press, 1947).

Received June 15, 1957

* In Russian.

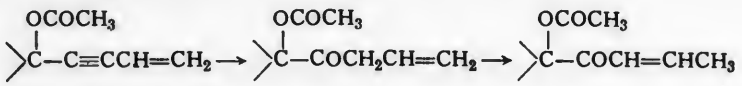
** Original Russian pagination. See C. B. Translation.

ACETYLENE DERIVATIVES

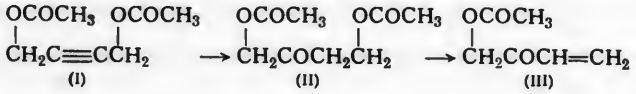
187. HYDRATION OF DIACETATES OF ACETYLENIC γ-GLYCOLS. SYNTHESIS OF UNSATURATED α-ACETOXYKETONES. III.

I. N. Nazarov* and S. G. Matsoyan

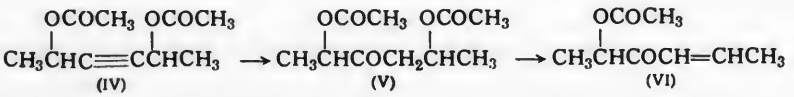
In previous communications we have shown that when acetates of vinylethynylcarbinols are hydrated in acetic acid solutions in the presence of mercuric acetate at 40-50°, good yields of allyl α-acetoxyketones are produced, which are easily isomerized by the action of mercury salts or of acid or alkaline reagents to the corresponding propenyl α-acetoxyketones [1].



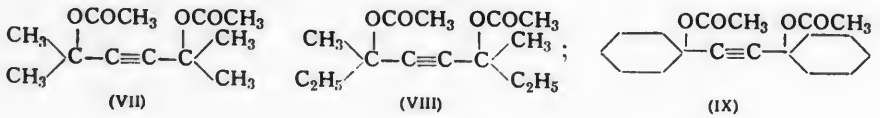
In the present investigation we have studied the hydration of diacetates of acetylenic γ-glycols, which was carried out in boiling, 90% acetic acid solutions in the presence of mercuric acetate. When the diacetate of butyn-1,4-diol (I) was hydrated under the above-described conditions, the diacetoxyketone (II) was formed in 55% yield and the α-acetoxyketone (III) was formed in 20% yield [2].



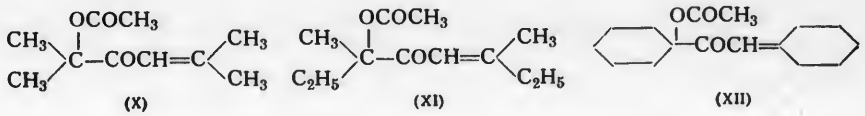
Hydration of the diacetate of 3-hexen-2,5-diol (IV) produced, in addition to the diacetoxyketone (V) (10% yield), mainly the unsaturated α-acetoxyketone (VI) (75% yield).



Hydration of the diacetates of the ditertiary acetylenic γ-glycols (VII, VIII, and IX) under similar conditions led to the formation only of the unsaturated α-acetoxyketones (X, XI, and XII) in good yields and did not produce the corresponding diacetoxyketones at all.



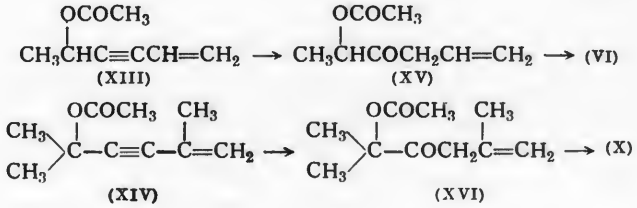
*Deceased.



(X) (XI) (XII)

The rate of hydration drops with an increase in the molecular weight of the acetylenic γ-glycol. The ease of splitting out acetic acid from the diacetates of 2-keto-1,4-diols depends on the character of the β-acetoxy group. Primary β-acetoxy groups are split out with difficulty under the hydration conditions, the splitting out of secondary β-acetoxy groups proceeds considerably more readily, and tertiary β-acetoxy groups are completely split out under the hydration conditions. It is interesting to note that the addition of acetic acid to α,β-unsaturated ketones in the presence of mercuric acetate shows the same dependence upon the degree of substitution [3]. When the diacetoxyketones (II) and (V) were heated in the presence of anhydrous sodium acetate or potassium bisulfate, splitting out of acetic acid occurred with the formation of the above-described unsaturated α-acetoxyketones (III) and (VI).

When the acetates of methylvinylethynylcarbinol (XIII) and dimethylisopropenylethynylcarbinol (XIV) were hydrated in acetic acid with the aid of mercuric acetate, the above-described unsaturated α-acetoxyketones (VI) and (X) also were formed. In this case we did not succeed in isolating the corresponding allylketones (XV) and (XVI), which are the primary hydration products. This is apparently explained by the fact that the hydration of the acetates (XIII) and XIV) proceeds only at higher temperatures (60-80°), i.e., under conditions that facilitate the isomerization of the allylketones (XV) and (XVI) to the propenylketones (VI) and (X).



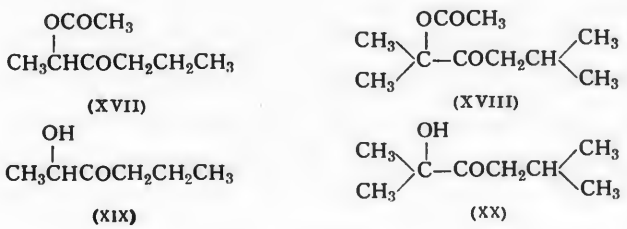
(XIII) (XV) (VI)

(XIV) (XVI) (X)

We attempted to prepare the allylketones (XV) and (XVI) by hydration of the acetates (XIII) and (XIV) in acetic acid at low temperature (30-45°) with the aid of mercury sulfate, but only the propenyl ketones (VI) and (X) were formed.

When the unsaturated α-acetoxyketone (X) was oxidized with potassium permanganate, as might be expected, acetone and the acetate of α-hydroxyisobutyric acid were obtained.

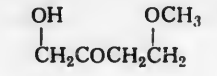
Hydrogenation of the unsaturated α-acetoxyketones (VI) and (X) in the presence of Pt catalyst produced the saturated α-acetoxyketones (XVII) and (XVIII), which were smoothly saponified by alcoholic alkali to the corresponding α-ketoalcohols (XIX) and (XX).



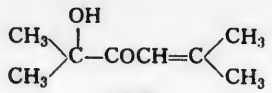
(XVII) (XVIII)

(XIX) (XX)

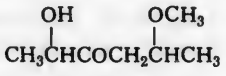
Transesterification of the unsaturated α-acetoxyketones (III), (VI), (X), and (XI) in methanol solution in the presence of catalytic amounts of sulfuric acid or alkali leads to the formation in the first two instances of the methoxyketoalcohols (XXI) and (XXII), and in the last case of the unsaturated α-ketoalcohols (XXIII) and (XXIV). These α-ketoalcohols also were produced in small yield by direct saponification of the unsaturated α-acetoxyketones (X) and (XI) with alcoholic alkali.



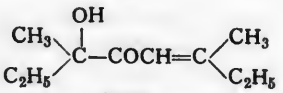
(XXI)



(XXIII)



(XXII)



(XXIV)

EXPERIMENTAL

The diacetates of the acetylenic γ-glycols were prepared by the method of Dupont by boiling the appropriate glycols with acetic anhydride in the presence of anhydrous sodium acetate [4].

Hydration of the diacetate of butyn-1,4-diol. A mixture of 38 g of the diacetate (I) (b. p. 102-104° at 3 mm, n_D^{20} 1.4535, m. p. 28-30°) [2, 4], 135 g of 90% acetic acid, and 6 g of mercuric acetate was refluxed for 3 hours. The acetic acid was distilled off in vacuo at 35-45°, and the residue was distilled in vacuo with an oil pump. After repeated redistillation of the product in vacuo, 5.5 g of the acetate of 1-buten-4-ol-3-one (III) with b. p. 75-76° (9 mm, n_D^{20} 1.4450 and 22.9 g of the diacetate of 2-butanon-1,4-diol (II) with b. p. 101-103° (1 mm), n_D^{20} 1.4410 were obtained [2].

The unsaturated α-acetoxyketone (III) was a mobile liquid with a sharply lachrymatory odor. Upon standing for several days, it polymerized to a colorless, gelatinous mass. The 2,4-dinitrophenylhydrazone of the α-acetoxyketone (III) melted at 108-109° (from alcohol).

Found %: N 18.21, 18.20. $C_{12}H_{12}O_6N_4$. Calculated %: N 18.18.

Splitting out of acetic acid from the diacetate of 2-butanon-1,4-diol (II). A mixture of 7 g of the diacetoxyketone (II), 0.3 g of finely ground, anhydrous potassium sulfate, and 0.005 g of pyrogallol was distilled on a metal bath (120-170°) in a vacuum of 11 mm. After repeated distillation in vacuo we obtained 0.9 g of acetic acid, 3 g of unsaturated α-acetoxyketone (with b. p. 80-82° at 11 mm, n_D^{20} 1.4455), the 2,4-dinitrophenylhydrazone of which melted at 108-109°, and 2 g of the starting diacetoxyketone (II) with b. p. 139-141° at 11 mm, n_D^{20} 1.4420.

Transesterification of the diacetate of 2-butanon-1,4-diol (II). A mixture of 15 g of the diacetoxyketone (II) and 80 g of methanol that contained 2 drops of concentrated sulfuric acid was refluxed for 15 hours. The methanol and methyl acetate were distilled off in vacuo and the residue was neutralized with sodium carbonate, extracted with ether, and dried with magnesium sulfate. Upon distillation we obtained 8 g of 1-methoxybutan-4-ol-3-one (XXI) with b. p. 56-57° at 2 mm, n_D^{20} 1.4365; the 2,4-dinitrophenylhydrazone melted at 228-230° [5]. Transesterification of the α-acetoxyketone (III) under similar conditions also produced 1-methoxybutan-4-ol-3-one.

Hydration of the diacetate of 3-hexyn-2,5-diol (IV). A mixture of 16 g of the diacetate (IV) with b. p. 75-79° at 2 mm, n_D^{20} 1.442 (in the stereoisomeric forms) [4], 70 g of 90% acetic acid, and 5 g of mercuric acetate was refluxed for 12 hours. The acetic acid was distilled off (35-45° at 25 mm) and the residue was distilled twice in vacuo. 9.5 g of the acetate of methylcrotonylcarbinol (VI) was obtained.

B. p. 55-57° (2 mm), 93-95° (12 mm), n_D^{20} 1.4465, d_4^{20} 1.0199, MR 40.88; calc. 40.34.

Found %: C 61.71, 61.36; H 7.41, 7.45. $C_8H_{12}O_3$. Calculated %: C 61.53; H 7.69.

The 2,4-dinitrophenylhydrazone of α-acetoxyketone (VI) melted at 125-127° (from a mixture of ethanol and ethyl acetate).

Found %; N 16.49, 16.74. $C_{14}H_{16}O_6N_4$. Calculated %: N 16.66.

In addition, we obtained from this experiment 1.7 g of the diacetate of 3-hexanon-2,5-diol (V).

B. p. 90-92° (2 mm), n_D^{20} 1.4375, d_4^{20} 1.0876. MR 52.13; calc. 51.70.

Found %: C 55.72, 55.68; H 7.65, 7.50. $C_{10}H_{16}O_5$. Calculated %: C 55.50; H 7.41.

Splitting out of acetic acid from the diacetate of 3-hexanon-2,5-diol (V). By distillation of 1 g of the diacetoxyketone (V) in the presence of anhydrous sodium acetate in vacuo (30-20 mm) on a metal bath (120-150°) we obtained 0.6 g of the acetate of methylcrotonylcarbinol (VI) with n_D^{20} 1.4470; the 2,4-dinitrophenylhydrazone melted at 125-127° and gave no depression with the specimen described above.

Hydration of the acetate of methylvinylethynylcarbinol (XIII). To a mixture of 1 g of mercury sulfate and 155 g of 96% acetic acid was added dropwise, over a period of 3 hours, at 35° and with continuous stirring, a solution of 30 g of acetate (XIII) (b. p. 64-65° at 11 mm, n_D^{20} 1.4620) [6] in 30 g of acetic acid. Then the reaction mixture was stirred at 35-45° for 4 hours. The acetic acid was distilled off in vacuo on a water bath (30-40°) and the residue was neutralized with sodium carbonate, extracted with ether, and dried with magnesium sulfate. We obtained 20.5 g of the acetate of methylcrotonylcarbinol (VI) with b. p. 91-94° at 11 mm, n_D^{20} 1.4470, the 2,4-dinitrophenylhydrazone of which melted at 125-127° and gave no depression with the specimen described above.

The hydration of the acetate of methylvinylethynylcarbinol (XIII) in acetic acid solution in the presence of mercuric acetate proceeded at 60-80° and also produced acetoxyketone (VI) in 40-50% yield.

Hydrogenation of the acetate of methylcrotonylcarbinol (VI). 5 g of α-acetoxyketone (VI) in solution in 15 ml of alcohol was hydrogenated in the presence of Pt catalyst. The theoretical amount of hydrogen required for one double bond was absorbed. The catalyst was filtered off, the alcohol was distilled off, and the product was distilled in vacuo. 4.5 g of the acetate of methylbutyrylcarbinol (XVII) was obtained.

B. p. 82-84° (11.5 mm), n_D^{20} 1.4205, d_4^{20} 0.9825, MR 40.76; calc. 40.81.

Found %: C 60.84, 60.86; H 8.85, 9.23. $C_8H_{14}O_3$. Calculated %: C 60.73; H 8.92.

Saponification of the acetate of methylbutyrylcarbinol (XVII). To a solution of 0.9 g of sodium hydroxide in 15 g of 90% alcohol was gradually added, with cooling, 3 g of the α-acetoxyketone (XVII). The reaction mixture was heated on a water bath for 1 hour, the alcohol was distilled off in vacuo, the residue was diluted with water, saturated with potassium carbonate, and the product was extracted with ether and dried with magnesium sulfate. 2.1 g of methylbutyrylcarbinol (XIX) was obtained.

B. p. 60-61° (11 mm), n_D^{20} 1.4245, d_4^{20} 0.9443, MR 31.43; calc. 31.44.

Found %: C 62.00, 62.01; H 10.26, 10.49. $C_6H_{12}O_2$. Calculated %: C 62.06; H 10.34.

The semicarbazone melted at 182-183° (from alcohol).

Found %: N 24.56, 24.59. $C_7H_{15}O_2N_3$. Calculated %: N 24.27.

Transesterification of the acetate of methylcrotonylcarbinol (VI). A mixture of 13 g of the α-acetoxyketone (VI) and 75 g of methanol that contained 2 drops of concentrated sulfuric acid was refluxed for 14 hours. The methanol and methyl acetate were distilled off and the residue was neutralized with sodium carbonate, extracted with ether, and dried with magnesium sulfate. 8.5 g of methyl-β-methoxybutyrylcarbinol (XXII) was obtained.

B. p. 48-50° (2 mm) n_D^{20} 1.4335, d_4^{20} 1.0078, MR 37.74; calc. 37.71.

Found %: C 57.65, 57.68; H 10.12, 10.15. $C_7H_{14}O_3$. Calculated %: C 57.50; H 9.91.

Hydration of the diacetate of 2,5-dimethyl-3-hexyn-2,5-diol (VII). A mixture of 55 g of the diacetate (VII) (b. p. 84-86° at 4 mm, 103-105° at 10 mm, n_D^{20} 1.4450) [4], 150 g of 90% acetic acid, and 5 g of mercuric acetate was refluxed for 22 hours. After this, 10 g more of mercuric acetate was introduced in small portions. The dark reaction product was poured off from the precipitated mercury, the acetic acid was distilled off (35-45° at 25 mm), and the residue was distilled in vacuo. After repeated distillation 34 g of the acetate of 2,5-dimethyl-4-hexen-2-ol-3-one (X) was obtained.

B. p. 90-92° (7 mm), 97-98° (10 mm), n_D^{20} 1.4610, d_4^{20} 0.9915, MR 50.97; calc. 49.57.

Found %: C 65.34, 64.88; H 9.16; 9.31. $C_{10}H_{16}O_3$. Calculated %: C 65.20; H 8.75.

The 2,4-dinitrophenylhydrazone melted at 105-107° (from a mixture of alcohol and ethyl acetate).

Found %: N 15.81; 16.03. $C_{16}H_{20}O_3N_4$. Calculated %: N 15.38.

Hydration of the acetate of dimethylisopropenylethynylcarbinol (XIV). To a solution of 4 g of mercuric acetate in 150 g of 90% acetic acid was added dropwise, over a period of 2 hours, at 40° with stirring, 45 g of the acetate (XIV) (b. p. 70-71° at 9.5 mm, n_D^{20} 1.4578) [6]. Then 3 g of mercuric acetate was introduced into the reaction mixture and stirring was continued at 45-65° for 5 hours. The acetic acid was distilled off (35-45° at 25 mm) and the residue was distilled in vacuo and a fraction collected with b. p. 85-100° at 100 mm. After repeated distillation of the product in vacuo we obtained 20.5 g of the acetate of 2,5-dimethyl-4-hexen-2-ol-3-one (X) with b. p. 95-97° at 10 mm, n_D^{20} 1.4605; the 2,4-dinitrophenylhydrazone melted at 105-107° and gave no depression with the specimen described above.

Hydrogenation of the acetate of 2,5-dimethyl-4-hexen-2-ol-3-one (X). 6.5 g of the α-acetoxyketone (X) dissolved in 20 ml of alcohol was hydrogenated in the presence of Pt catalyst. The theoretical amount of hydrogen required for one double bond was absorbed. 6 g of the acetate of 2,5-dimethylhexan-2-ol-3-one (XVIII) was obtained.

B. p. 85-87° (10 mm), n_D^{20} 1.4295, d_4^{20} 0.9524, MR 50.44; calc. 50.04.

Found %: C 64.82; 64.75; H 10.00, 9.85. $C_{10}H_{18}O_3$. Calculated %: C 64.50; H 9.74.

Saponification of the acetate of 2,5-dimethylhexan-2-ol-3-one (XVIII). By the saponification of 3.5 g of the α-acetoxyketone (XVIII) with a solution of 0.8 g of sodium hydroxide in 10 ml of 90% alcohol we obtained 2.2 g of 2,5-dimethylhexan-2-ol-3-one (XX) with b. p. 65-66° at 10 mm, n_D^{20} 1.4275; the semicarbazone melted at 143-145° [7].

Transesterification of the acetate of 2,5-dimethyl-4-hexen-2-ol-3-one (X). A solution of 15 g of the α-acetoxyketone (X) in 75 g of methanol containing 0.3 g of potassium hydroxide was refluxed for 10 hours. The methanol and methyl acetate were distilled off in vacuo and the residue was diluted with water, saturated with potassium carbonate, extracted with ether, and dried with magnesium sulfate. 9.8 g of 2.5-dimethyl-4-hexen-2-ol-3-one (XXIII) was obtained.

B. p. 74-75° (10 mm), n_D^{20} 1.4650, d_4^{20} 0.9461, MR 41.55; calc. 40.21 [7].

Found %: C 67.29, 67.28; H 10.26, 10.00. $C_8H_{14}O_2$. Calculated %: C 67.56; H 9.92.

Upon acetylation of the α-ketoalcohol (XXIII) that was obtained above with acetic anhydride in the presence of traces of sulfuric acid, we obtained the starting α-acetoxyketone (X).

Oxidation of the acetate of 2,5-dimethyl-4-hexen-2-ol-3-one (X). 16.5 g of finely ground potassium permanganate was introduced in small portions, with vigorous stirring and cooling with ice water, into a mixture of 9.6 g of the acetate of 2,5-dimethyl-4-hexen-2-ol-3-one (X) and 200 ml of water. On the following day the precipitate of manganese dioxide was filtered out. To 5 ml of the filtrate was added an acidified alcoholic solution of 2,4-dinitrophenylhydrazine. The precipitate that formed melted, after recrystallization from alcohol, at 125-126° and gave no depression with the 2,4-dinitrophenylhydrazone of acetone.

The water was distilled off from the filtrate in vacuo on a water bath at 30-40° and the residue, after acidification with concentrated hydrochloric acid, was carefully extracted with ether. 3.6 g of the acetate of α-hydroxyisobutyric acid was obtained with b. p. 101-104° at 3 mm, n_D^{20} 1.4290; upon the saponification of this acetate with alcoholic alkali, α-hydroxyisobutyric acid with m. p. 79-80° (from benzene) was isolated [8].

Hydration of the diacetate of 3,6-dimethyl-4-octyn-3,6-diol (VIII). A mixture of 65 g of the diacetate (VIII) (b. p. 114-121° at 10 mm in the stereoisomeric forms) [4], 200 g of 90% acetic acid, and 16 g of mercuric acetate was refluxed for 25 hours. After two fractional distillations of the reaction mixture, 43 g of the acetate of 3,6-dimethyl-5-octen-3-ol-4-one (XI) was obtained.

B. p. 80-82° (1 mm), 115-118° (10 mm) n_D^{20} 1.4635, d_4^{20} 0.9741, MR 58.81; calc. 60.05.

Found %: C 67.32, 67.33; H 9.53, 9.78. $C_{12}H_{20}O_3$. Calculated %: C 67.88; H 9.49.

The 2,4-dinitrophenylhydrazone melted at 130-132° (from a mixture of alcohol and ethyl acetate).

Transesterification of the acetate of 3,6-dimethyl-5-octen-3-ol-4-one (XI). A solution of 35 g of α-acetoxyketone (XI) in 135 g of methanol containing 3 g of potassium hydroxide was refluxed for 10 hours. The methanol was distilled off in vacuo. The residue was extracted with ether, the ethereal extract was washed with water and dried with magnesium sulfate. 19.5 g of 3,6-dimethyl-5-octen-3-ol-4-one (XXIV) was obtained.

B. p. 94-96° (10 mm), n_D^{20} 1.4640, d_4^{20} 0.9281, MR 50.60; calc. 49.45.

Found %: C 69.82, 69.98; H 10.45, 10.66. $C_{10}H_{18}O_2$. Calculated %: C 70.58; H 10.58.

Upon acetylation with acetic anhydride of the α-ketoalcohol (XXIV) thus obtained, the starting α-acetoxyketone (XI) was produced.

Hydration of the diacetate of bis-(1-hydroxycyclohexyl) acetylene (IX). A mixture of 28 g of the diacetate (IX) (b. p. 140-145° at 2 mm, n_D^{20} 1.4965, m. p. 45-46°) [4], 100 g of 90% acetic acid, and 8 g of mercuric acetate was refluxed for 30 hours. By vacuum distillation of the reaction mixture, 19 g of the unsaturated α-acetoxyketone (XII) was obtained as a viscous liquid with b. p. 129-131° at 1.5 mm, n_D^{20} 1.5215.

Found %: C 73.14, 73.26; H 9.28, 9.34. $C_{16}H_{24}O_3$. Calculated %: C 72.71; H 9.15.

The 2,4-dinitrophenylhydrazone of the α-acetoxyketone (XII) melted at 127-129° (from ethyl acetate).

SUMMARY

1. By the hydration of the diacetates of acetylenic γ-glycols in boiling acetic acid solution in the presence of mercuric acetate, the diacetates of the corresponding 2-keto-1,4-diols are formed, which split out the β-acetoxy group to form the unsaturated α-acetoxyketones.

The ease of splitting out acetic acid from the diacetates of the 2-keto-1,4-diols depends on the character of the β-acetoxy group. The most easily split out are the tertiary β-acetoxy groups, and the most difficult to split out are the primary β-acetoxy groups.

2. Some transformations of the unsaturated α-acetoxyketones and diacetoxyketones obtained have been studied.

LITERATURE CITED

[1] I. N. Nazarov and S. G. Matsoyan, J. Gen. Chem. 27, 2115, 2128 (1957).*

[2] Lozach, Bull. Soc. Chim. 11, 514 (1944).

[3] I. N. Nazarov, S. G. Matsoyan and S. A. Vartanyan, J. Gen. Chem. 27, 1818 (1957).*

[4] Dupont, Bull. Soc. Chim. 1949, 789; 1951, 755; J. Gen. Chem. 5, 1723 (1935); Ann. Chim. (8), 30, 485 (1913).

[5] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 3, 287 (1949); Yu. K. Yuryev et al., Proc. Acad. Sci. USSR, 62, 645 (1948).

[6] I. N. Nazarov and A. N. Elizarova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 2, 190 (1940).

[7] V. N. Krestinsky and L. N. Bazhenova-Kozlovskaya, J. Gen. Chem. 2, 829 (1932).

[8] Dictionary of Org. Compds., II, 277.*

Received October 15, 1956

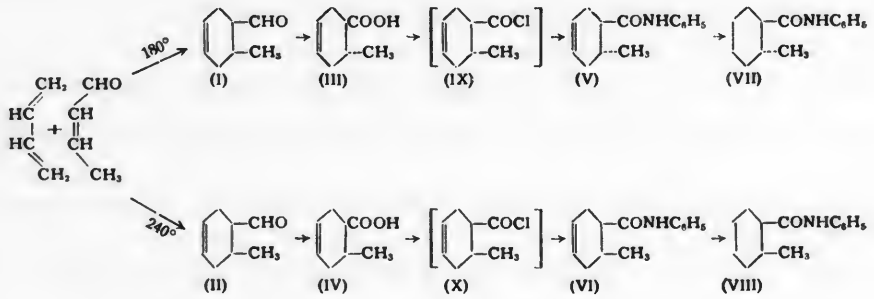
Institute of Organic Chemistry of
The Academy of Sciences of the USSR and
Chemical Institute of the Academy of Sciences
Armenian SSR

*Original Russian pagination. See C. B. Translation.

GEOMETRIC ISOMERISM OF Δ^3-TETRAHYDROTOLUALDEHYDE

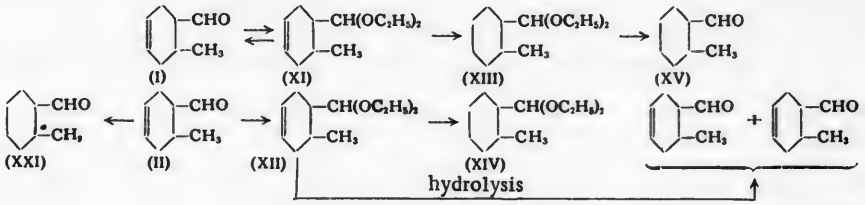
I. N. Nazarov, G. P. Kugatova and V. V. Mozolis

The condensation of bivinyl with trans-crotonaldehyde was first carried out by Diels and Alder [1] and later was studied by other authors [2, 3]. This condensation usually has been carried out at temperatures of 150-180° and under these conditions yielded trans-Δ^3-tetrahydrotolualdehyde (I). In a detailed study of the condensation of bivinyl with trans-crotonaldehyde we have established that the previously described trans-Δ^3-tetrahydrotolualdehyde (I) is formed only at temperatures below 200°, while at 240° this condensation results predominantly in the formation of cis-Δ^3-tetrahydrotolualdehyde (II) with a higher index of refraction. The trans-aldehyde (I) readily yields a semicarbazone with m. p. 168-169° and a 2,4-dinitrophenylhydrazone with m. p. 161-162°, but the cis-aldehyde (II) under the same conditions is largely isomerized and also yields derivatives of the trans-aldehyde. However, we succeeded in isolating from the filtrates in 15% yield a semicarbazone and a 2,4-dinitrophenylhydrazone that corresponded to the cis-aldehyde (II) and melted at 180-181° and 134-135° respectively. Oxidation of the trans-aldehyde (I) both with silver nitrate and with the oxygen of the air produced the known trans-Δ^3-tetrahydrotoluic acid (III) with m. p. 68°. Oxidation of the cis-aldehyde (II) with the oxygen of the air yielded the liquid cis-acid (IV).



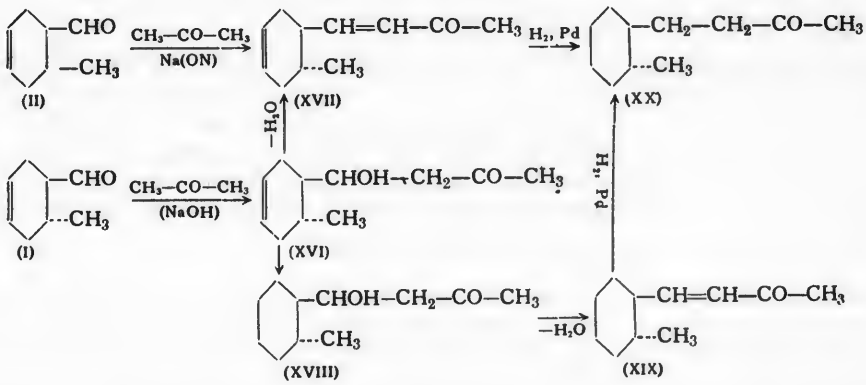
By treatment of the isomeric acids (III) and (IV) with oxalyl chloride at room temperature we obtained the corresponding acid chlorides (IX) and (X) which, without distillation, were converted by reaction with aniline at −5° to the anilides. Thus we obtained from the trans-acid (III) the trans-anilide (V) with m. p. 114-115°, and from the cis-acid (IV) the cis-anilide (VI) with m. p. 95-97°. By hydrogenation over a Pd catalyst the isomeric anilides (V) and (VI) were converted to the known saturated trans- and cis-anilides (VII) and (VIII), which melted at 151-152° and 128-130° [2] respectively. When the pure trans- and cis-aldehydes were heated in metal ampoules at 250-260° for 3-4 hours, in both cases an identical mixture of these aldehydes was obtained with n_D^{20} 1.4680, containing about 1/4 cis-aldehyde (II) and 3/4 trans-isomer (I). Consequently, both of these aldehydes are capable of reversible thermal isomerization, which probably explains the above-mentioned dependence of their formation on the temperature at which the condensation of bivinyl with crotonaldehyde is carried out. In the presence of acids, the pure cis-aldehyde (II) is isomerized even at room temperature to the trans-aldehyde (I); however, in this case, as in thermal isomerization, the mixture of the cis- and trans-forms of Δ^3-tetrahydrotolualdehyde is produced that has been noted above in the preparation of the semicarbazone and 2,4-dinitrophenylhydrazone. From this mixture with n_D^{20} 1.4680 we again separated by chromatography on Al_2O_3 the pure cis-aldehyde with n_D^{20} 1.4700 and trans-aldehyde with n_D^{20} 1.4653 in the ratio 1 : 3.

From the isomeric aldehydes (I) and (II) under mild conditions we succeeded in preparing the corresponding diethylacetals (XI) and (XII), which were converted by hydrogenation with a palladium catalyst to the corresponding saturated diethylacetals (XIII) and (XIV). Hydrolysis of the acetals (XI) and (XIII) produced the trans-aldehydes (I) and (XV); hydrolysis of the cis-diethylacetal (XII) yielded a mixture of the two aldehydes (I) and (II) with n_D^{20} 1.4680 and consequently also was accompanied by cis-trans-isomerization. By hydrogenation of the unsaturated cis-aldehyde (II) with Pd catalyst the cis-aldehyde (XXI) was obtained.



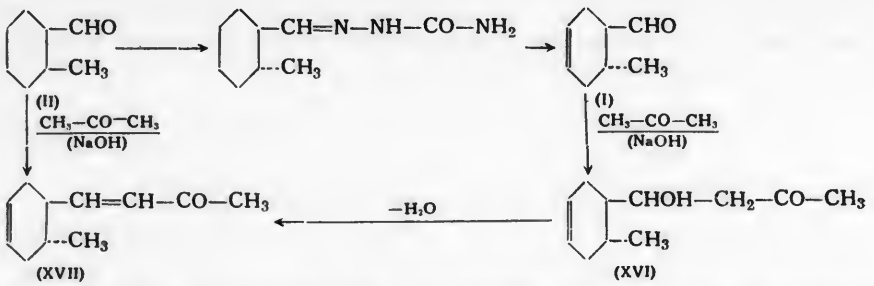
The trans-aldehyde (XV) was obtained also by the hydrogenation of the unsaturated trans-aldehyde (I) in the presence of Pd catalyst.

It was of interest to investigate the behavior of the trans- and cis-aldehydes (I) and (II) in the condensation reaction with acetone, since the products of this reaction are analogs of β-ionone and can be further utilized in the synthesis of analogs of vitamin A. It was found that in the condensation reaction with acetone, which was carried out at low temperature in the presence of the dilute solutions of sodium hydroxide, the trans- and cis-forms of Δ^3-tetrahydrotolualdehyde behave differently. While the trans-aldehyde (I), as a result of aldol condensation, gives the stable ketoalcohol (XVI) in 68% yield, the cis-aldehyde (II) upon similar condensation yields only the product of crotonic condensation (XVII).

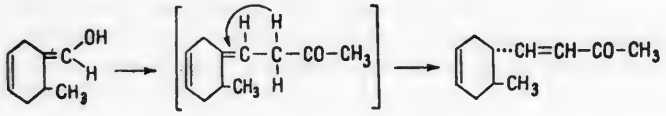


The ketoalcohol (XVI) is readily dehydrated by heating with potassium bisulfate at 130-140° to the corresponding unsaturated ketone (XVII), which is obtained as described above by direct condensation of the cis-aldehyde (II) with acetone. Upon hydrogenation of the ketone (XVII) over palladium catalyst, 2 moles of hydrogen were absorbed and the known [4] saturated ketone (XX) was producted, which also was obtained from the ketoalcohol (XVI) by hydrogenation to the saturated ketoalcohol (XVIII), dehydration of this to the ketone (XIX), and rehydrogenation of the latter. The behavior of the trans- and cis-aldehydes (I) and (II) in the condensation reaction with acetone that has been mentioned was made especially clear by the following experiment:

20 g of cis-aldehyde (II) (n_D^{20} 1.4700) was divided in half. One half was condensed with acetone and yielded the ketone (XVII), and from the other half a semicarbazone was prepared, most of which melted at 168-169°, corresponding to the trans-form. After decomposition of the semicarbazone the trans-aldehyde (I) (n_D^{20} 1.4652) was isolated, which upon condensation with acetone yielded the ketoalcohol (XVI), the dehydration of which produced the unsaturated ketone (XVII).



Such differences in the behavior of the trans- and cis-aldehydes (I) and (II) in this condensation with acetone can be explained by the assumption that the cis-arrangement of the ortho-methyl group in aldehyde (II) facilitates the enolization of the latter. Then the mechanism of the condensation of the cis-aldehyde (II) with acetone can be represented as proceeding through its enol form with the formation of an intermediate product (shown in brackets) in which an allyl rearrangement to the energetically more advantageous trans-configuration immediately occurs.



EXPERIMENTAL

Trans-Δ^3-tetrahydrotolualdehyde (I). 17 g of trans-crotonaldehyde (b. p. 101-103°, n_D^{20} 1.4365), 13 g of freshly distilled bivinyl, and a small amount of hydroquinone were placed in a methyl ampoule. The ampoule was heated for 2 hours at 190-200° and the reaction product was distilled in vacuo. 10.4 g of aldehyde (I) was obtained with b. p. 70-72° at 19 mm, n_D^{20} 1.4648. 136 g of this aldehyde collected from several experiments was redistilled in vacuo and 116 g of pure aldehyde (I) was isolated by this process with b. p. 59° at 10 mm, n_D^{20} 1.4652, the semicarbazone of which melted in agreement with the literature data [1] at 168-169° (from methanol).

Found %: N 23.33, 23.11. $C_9H_{15}ON_3$. Calculated %: N 23.2.

A mixture of 10 g of the semicarbazone of the trans-aldehyde (I), 50 ml of 2 N sulfuric acid, and 50 ml of petroleum ether (b. p. up to 60°) was boiled for 2 hours until solution was complete. The product was extracted with ether, washed with sodium carbonate solution, dried with calcium chloride, and distilled in vacuo. 5.3 g of aldehyde (I) was obtained with b. p. 69° at 19 mm, n_D^{20} 1.4653. The 2,4-dinitrophenylhydrazone melted at 158-159° (from ethanol).

Cis-Δ^3-tetrahydrotolualdehyde (II). 32 g of trans-crotonaldehyde, 25 g of freshly distilled bivinyl, and a small amount of hydroquinone were placed in a metal ampoule. The ampoule was heated for 2 hours at 240-242°, after which the condensation product was distilled in vacuo. After two distillations, 16.6 g of aldehyde (II) was obtained with b. p. 71-72° at 18 mm, n_D^{20} 1.4700.

Found %: C 77.09, 77.01; H 9.71, 9.74. $C_8H_{12}O$. Calculated %: C 77.41; H 9.68.

The semicarbazone melted at 180-181° (from methanol).

Found %: N 23.01, 23.1. $C_9H_{15}ON_3$. Calculated %: N 23.2.

The 2,4-dinitrophenylhydrazone melted at 134-135° (from ethanol). In the preparation of the semicarbazone and the 2,4-dinitrophenylhydrazone, the cis-aldehyde (II) was in large part isomerized and yielded derivatives of the trans-isomer (I). However, by evaporating the filtrates in vacuo and washing the residues with cold solvent, we were able to also isolate the above-described derivatives of the cis-aldehyde (II).

To a solution of 10 g of cis-aldehyde (II) in 20 ml of methanol was added a solution of semicarbazide acetate prepared from 10 g of potassium acetate and 11 g of semicarbazide hydrochloride in 20 ml of methanol. The precipitate that separated was filtered off and in this way 13 g of a mixture of semicarbazones with m.p. 148-164° was obtained. After two recrystallizations from methanol, 10 g of the semicarbazone of the trans-aldehyde (I) was isolated with m. p. 168-169°. From the filtrates, 2.4 g of the semicarbazone of the cis-aldehyde (II) with m. p. 180-181° was isolated. A sample of a mixture of these semicarbazones melted at 153-158°. A sample of a mixture of the 2,4-dinitrophenylhydrazones of the isomeric aldehydes (I) and (II) melted at 127-132°.

Isomerization of trans-Δ^3-tetrahydrotolualdehyde (I). 10 g of the trans-aldehyde (I) (b. p. 73° at 18 mm, n_D^{20} 1.4652) was heated in a metal ampoule at 260-270° for 4 hours. After distillation in vacuo 9 g of a mixture of the cis- and trans-forms was obtained with b. p. 68-69° at 17 mm, n_D^{20} 1.4680.

Isomerization of cis-Δ^3-tetrahydrotolualdehyde (II). a) 5 g of the cis-aldehyde (II) (b. p. 72-73° at 18 mm, n_D^{20} 1.4700) was heated in a metal ampoule at 260-270° for 4 hours. After distillation in vacuo 3.9 g of a mixture of the cis- and trans-forms was obtained with b. p. 68° at 17 mm, n_D^{20} 1.4680.

b) A mixture of 11 g of the cis-aldehyde (II) (b. p. 72-73° at 18 mm, n_D^{20} 1.4700) and 40 ml of 40% sulfuric acid was left at room temperature for 30 hours (the mixture was shaken periodically), after which the product was extracted with ether, washed with sodium carbonate solution, then with water, dried with magnesium sulfate, and distilled in vacuo. 9.5 g of a mixture of the cis- and trans-aldehydes (I) and (II) was obtained with b. p. 70-72° at 18 mm, n_D^{20} 1.4680, from which there were separated by chromatography on Al_2O_3 (diameter of column 1.5 cm and height 10 cm) the pure cis-aldehyde (2.1 g) with n_D^{20} 1.4700 and the trans-aldehyde (6.5 g) with n_D^{20} 1.4653. All the fractions with n_D^{20} 1.4680 obtained from the above-described isomerization were combined, and from the mixture a sample was taken for analysis.

Found %: C 77.20, 77.14; H 9.95, 9.82. $C_8H_{12}O$. Calculated %: C 77.4; H 9.7.

Trans-Δ^3-tetrahydrotoluic acid (III). a) A mixture of 6 g of the trans-aldehyde (I) with two drops of water was placed in a porcelain dish and allowed to stand in the air. In 2 weeks, crystals appeared in the liquid, and in a month it had completely crystallized. The crystals were treated with sodium carbonate solution, the soda solution was acidified with hydrochloric acid and extracted with ether. The ether extract was washed with water and dried with magnesium sulfate. After the ether was distilled off, 5.7 g of the crystalline trans-acid (III) was obtained with m. p. 64°. After recrystallization from a mixture of ether and petroleum ether the acid (III) melted at 67-68°.

b) A solution of 7.5 g of the trans-aldehyde (I) in 15 ml of alcohol was mixed with an aqueous solution of 30 g of silver nitrate. A solution of 9 g of sodium hydroxide in 150 ml of water was added to the reaction mixture from a dropping funnel at 50° while stirring. The mixture was stirred at room temperature for 40 hours, after which the precipitate was filtered off and the aqueous extract was acidified with sulfuric acid. The product was extracted with ether, dried with magnesium sulfate, and distilled in vacuo. 3.2 g of the acid (III) was obtained with b. p. 98° at 1 mm, n_D^{15} 1.4789, which quickly crystallized and after recrystallization from aqueous methanol melted at 68° and gave no depression with the previous sample.

Cis-Δ^3-tetrahydrotoluic acid (IV). 6 g of the cis-aldehyde (II) was oxidized with the oxygen of the air, as described in the preceding experiment. In 2 weeks the liquid started to thicken, and in a month it was converted to a thick, oily mass, which was treated with a sodium carbonate solution. The soda solution was acidified with hydrochloric acid, the product was extracted with ether, dried with magnesium sulfate, and distilled in vacuo. 3 g was obtained of the liquid acid (IV) with b. p. 95-96° at 1 mm, n_D^{18} 1.4817.

Found %: C 68.26, 68.54; H 8.89, 8.72. $C_8H_{12}O_2$. Calculated %: C 68.57; H 8.57.

Anilide of trans-Δ^3-tetrahydrotoluic acid (V). 1 ml of oxalyl chloride was added to a solution of 1 g of the trans-acid (III) in 10 ml of anhydrous benzene, and the mixture was left at room temperature for 4 hours. The solvent and the excess oxalyl chloride were distilled off in vacuo. The acid chloride (X) that had been formed was dissolved, without distillation, in 10 ml of absolute ether and to the solution was slowly added, with stirring and cooling to −5°, a solution of 1 g of aniline in 10 ml of absolute ether. In 30 minutes, after stirring at 0°, water was added, the ether layer was separated, washed with 5% hydrochloric acid solution, 10% sodium carbonate solution, and water, and dried with calcium chloride. After the ether was distilled off, a crystalline product remained with m. p. 113-115°. After the recrystallization from a mixture of ether and petroleum ether, 0.6 g of the trans-anilide (V) was obtained with m. p. 114-115°.

Found %: C 78.06, 77.89; H 8.01, 8.05; N 6.48. $C_{14}H_{17}ON$. Calculated %: C 78.14; H 7.9; N 6.51.

Anilide of cis-Δ^3-tetrahydrotoluic acid (VI). In a manner similar to the preceding experiment there was prepared from 1 g of the liquid cis-acid (IV) 0.5 g of the crystalline cis-anilide (VI), which melted at 95-97° after recrystallization from a mixture of ether and petroleum ether.

Found %: C 78.23; H 8.15; N 6.75. $C_{14}H_{17}ON$. Calculated %: C 78.14; H 7.9; N 6.51.

Anilide of trans-hexahydrotoluic acid (VII). 200 mg of the unsaturated trans-anilide (V) was hydrogenated in solution in 30 ml of methyl alcohol with Pd catalyst. In 30 minutes 1 mole of hydrogen was absorbed. The catalyst was filtered out, the solvent was distilled off, and the crystalline residue was recrystallized from a mixture of ether and petroleum ether. 150 mg of the saturated trans-anilide (VII) was obtained, which melted at 151-152°.

Found %: C 77.60, 77.38; H 8.87, 8.94; N 6.43, 6.35. $C_{14}H_{19}ON$. Calculated %: C 77.41; H 8.75; N 6.45.

Anilide of cis-hexahydrotoluic acid (VIII). 70 mg of the unsaturated cis-anilide (VI) was hydrogenated in solution in 10 ml of methanol with Pd catalyst deposited on $CaCO_3$. In 30 minutes 1 mole of hydrogen was absorbed. By the treatment described above, 50 mg of the saturated cis-anilide (VIII) was obtained, which melted at 128-130° after recrystallization from a mixture of ether and petroleum ether.

Found %: C 77.30; H 8.79; N 6.58. $C_{14}H_{19}ON$. Calculated %: C 77.41; H 8.75; N 6.45.

Diethylacetal of trans-Δ^3-tetrahydrotolualdehyde (XI). To a solution of 20 g of trans-aldehyde (I) in 80 ml of absolute alcohol was added 0.5 ml of hydrochloric acid (d 1.21). The reaction mixture was left for 2 days at room temperature, after which it was poured into a solution of 2 g of sodium carbonate in 150 ml of water. The oil that separated was extracted with ether, dried with magnesium sulfate, and distilled twice in vacuo. 11.8 g of the trans-diethylacetal (XI) was obtained with b. p. 103-104° at 13 mm, n_D^{16} 1.4528.

Found %: C 72.62, 72.42; H 11.1, 11.09. $C_{12}H_{22}O_2$. Calculated %: C 72.72; H 11.11.

Hydrolysis of trans-diethylacetal (XI). 5 g of (XI) (b. p. 103-104°, n_D^{16} 1.4528) was mixed with 5 ml of acetic acid and 13 ml of 15% sulfuric acid. The mixture was refluxed for 5 hours. The product was extracted with ether, washed with sodium carbonate solution and with water, dried with magnesium sulfate, and distilled in vacuo. 2 g of the trans-aldehyde (I) was obtained with b. p. 61-62° at 13 mm, n_D^{20} 1.4653. The semicarbazone melted at 168-169° (from methanol).

Diethylacetal of cis-Δ^3-tetrahydrotolualdehyde (XII). To a solution of 5 g of the cis-aldehyde (II) (b. p. 68° at 14 mm, n_D^{20} 1.4700) in 20 ml of anhydrous alcohol was added 0.12 ml of hydrochloric acid (d 1.21). The reaction mixture was left for 2 days at room temperature, after which it was poured into a solution of 0.5 g of sodium carbonate in 150 ml of water. The oil that separated was extracted with ether, dried with magnesium sulfate, and distilled twice in vacuo. 2.7 g of (XII) was obtained with b. p. 108-109° at 16 mm, n_D^{18} 1.4578.

Found %: C 72.48, 72.59; H 10.94, 11.33. $C_{12}H_{22}O_2$. Calculated %: C 72.72; H 11.11.

Hydrolysis of cis-diethylacetal (XII). 8.8 g of (XII) was mixed with 10 ml of acetic acid and 20 ml of 15% sulfuric acid. The mixture was refluxed for 5 hours. After the usual treatment, 3.5 g of product was obtained with b. p. 73-74° at 18 mm, n_D^{20} 1.4680.

Diethylacetal of trans-hexahydrotolualdehyde (XIII). 23 g of the unsaturated trans-diethylacetal (XI) was hydrogenated in solution in 50 ml of methyl alcohol with Pd catalyst. In 3 hours, 2.7 g of hydrogen was absorbed which corresponds to the hydrogenation of one double bond. The catalyst was filtered out, the solvent was distilled off, and the product of hydrogenation was distilled in vacuo. 20.6 g of the saturated trans-diethylacetal (XIII) was obtained with b. p. 100° at 12 mm, n_D^{16} 1.4432.

Found %: C 71.96, 72.12; H 12.12, 12.12. $C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00.

Hydrolysis of trans-diethylacetal (XIII). 20 g of (XIII) was mixed with 20 ml of acetic acid and 50 ml of 15% sulfuric acid. The mixture was refluxed for 5 hours, after which the product was extracted with ether, washed with sodium carbonate solution and with water, dried with magnesium sulfate, and distilled in vacuo. 7.8 g of the trans-aldehyde (XV) was obtained with b. p. 58-59° at 11 mm, n_D^{18} 1.4484. The semicarbazone melted at 141-142°.

Found %: N 22.87, 22.88. $C_9H_{17}ON_3$. Calculated %: N 22.95.

Diethylacetal of cis-hexahydrotolualdehyde (XIV). 1 g of cis-unsaturated diethylacetal (XII) was hydrogenated in solution in 5 ml of methyl alcohol with Pd catalyst. In 2 hours 0.11 liters of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered out, the solvent was distilled off, and the product of hydrogenation was distilled in vacuo. 0.75 g of the saturated cis-diethylacetal (XIV) was obtained with b. p. 99° at 14 mm, n_D^{19} 1.4440.

Found %: C 71.83, 71.88; H 11.96, 11.97. $C_{12}H_{24}O$. Calculated %: C 72.00; H 12.00.

Trans-hexahydrotolualdehyde (XV). 20 g of the trans-aldehyde (I) was hydrogenated in solution in ethyl acetate with Pd catalyst, deposited on $CaCO_3$. In view of the fact that the hydrogenation proceeded slowly and with frequent additions of catalyst, it was not possible to account exactly for the amount of hydrogen absorbed. The hydrogenation lasted 48 hours. The catalyst was filtered out, the solvent was distilled off, and the hydrogenation product was distilled in vacuo. 18.2 g of the trans-aldehyde (XV) was obtained with b. p. 61-63° at 14 mm, n_D^{20} 1.4475. The semicarbazone melted at 141-142° (from methanol).

Cis-hexahydrotolualdehyde (XXI). 4 g of the cis-aldehyde (II) was hydrogenated in solution in 20 ml of methanol with Pd catalyst. In 5 hours 0.7 liters of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered out, the solvent was distilled off, and the hydrogenation product was distilled in vacuo. 2.8 g of the cis-aldehyde (XXI) was obtained with b. p. 67° at 16 mm, n_D^{29} 1.4522.

Found %: C 75.88, 75.98; H 10.95, 11.03. $C_8H_{14}O$. Calculated %: C 76.19; H 11.11.

Condensation of trans-Δ^3-tetrahydrotolualdehyde (I) with acetone. 20 g of the trans-aldehyde (I) (b. p. 59° at 10 mm, n_D^{20} 1.4652) was dissolved in 40 ml of freshly distilled acetone, and to the solution was added, at −1° with vigorous stirring, over a period of 13 minutes, 1.93 g of sodium hydroxide dissolved in a mixture of 154 ml of acetone and 62 ml of water. After this, stirring was continued for 75 minutes more at room temperature. The reaction mixture was poured into water that had been acidified with sulfuric acid. The product was extracted with ether, washed twice with water, dried with magnesium sulfate, and distilled in vacuo. 13 g of the trans-ketoalcohol (XVI) was obtained with b. p. 117-118° at 2 mm, n_D^{21} 1.4903.

Found %: C 72.49, 72.24; H 9.78, 9.98. $C_{11}H_{18}O_2$. Calculated %: C 72.53; H 9.89.

Condensation of cis-Δ^3-tetrahydrotolualdehyde with acetone. 20 g of the cis-aldehyde (II) (b. p. 73-74° at 19 mm, n_D^{20} 1.4700) was dissolved in 40 ml of freshly distilled acetone, and to the solution was added, at −5° and with vogorous stirring, over a period of 15 minutes, 1.93 g of sodium hydroxide dissolved in a mixture of 154 ml of acetone and 62 ml of water. After this, stirring was continued for 80 minutes more. By treatment as described above, 18 g of the trans-ketone (XVII) was obtained with b. p. 85-86° at 1 mm, n_D^{20} 1.4972.

Found %: C 80.37, 80.30; H 10.05, 9.97. $C_{11}H_{16}O$. Calculated %: C 80.37; H 9.81.

The semicarbazone melted at 149-150° (from methanol). The 2,4-dinitrophenylhydrazone melted at 155-156° (from ethanol).

Dehydration of trans-ketoalcohol (XVI). A mixture of 5 g of the unsaturated ketoalcohol (XVI) and 0.5 g of calcined, powdered potassium bisulfate was heated in a vacuum of 60 mm at 135-140° for 30 minutes. At the end of the heating period the vacuum was increased and the dehydration product was distilled. 3.8 g of the unsaturated ketone (XVII) was obtained with b. p. 92° at 1.5 mm, n_D^{18} 1.4980. The semicarbazone melted at 149-150° (from methanol). The 2,4-dinitrophenylhydrazone melted at 155-156° (from ethanol).

Hydrogenation of trans-ketoalcohol (XVI). 5 g of the trans-ketoalcohol (XVI) was hydrogenated in solution in 15 ml of methyl alcohol with Pd catalyst. In 2 hrs, 0.62 liters of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered out, the solvent was distilled off, and the hydrogenation product was distilled in vacuo. 3.7 g of the trans-ketoalcohol (XVIII) was obtained with b. p. 103° at 1 mm n_D^{15} 1.4744.

Found %: C 72.09, 71.77; H 11.11, 10.97. $C_{11}H_{20}O_2$. Calculated %: C 71.74; H 10.87.

The semicarbazone melted at 174-175° (from methanol).

Found %: N 17.39, 17.42. $C_{12}H_{23}O_2N_3$. Calculated %: N 17.42.

Dehydration of ketoalcohol (XVIII). A mixture of 5 g of ketoalcohol (XVIII) and 0.5 g of calcined, powdered potassium bisulfate was heated in vacuo for 30 minutes at 130-135°. At the end of the heating period the vacuum was increased and the product was distilled. 4.1 g of the ketone (XIX) was obtained with b. p. 81° at 1 mm, n_D^{14} 1.4815.

Found %: C 79.22, 79.42; H 10.66, 11.15. $C_{11}H_{18}O$. Calculated %: C 79.52; H 10.84.

The semicarbazone melted at 129-130° (from methanol).

Found %: N 18.63, 18.75. $C_{12}H_{21}ON_3$. Calculated %: N 18.83.

Hydrogenation of trans-ketone (XVII). 5 g of ketone (XVII) was hydrogenated in solution in 15 ml of methyl alcohol with Pd catalyst supported on calcium carbonate. In 3 hrs. 1.25 liters of hydrogen was absorbed, which corresponds to the hydrogenation of two double bonds. The catalyst was filtered out, the solvent was distilled off, and the hydrogenation product was distilled in vacuo. 4.2 g of the trans-keto (XX) was obtained with b. p. 77° at 2 mm, n_D^{14} 1.4645.

Found %: C 78.29, 78.26; H 11.79, 11.78. $C_{11}H_{20}O$. Calculated %: C 78.57; H 11.9.

The semicarbazone melted at 173-174°.

Found %: N 18.56, 18.51. $C_{12}H_{23}ON_3$. Calculated %: N 18.56.

Hydrogenation of trans-ketone (XIX). 2 g of trans-ketone (XIX) was hydrogenated in solution in 7 ml of methanol with Pd catalyst. In 1 hr, 0.3 liter of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered out, the solvent was distilled off, and the hydrogenation product was distilled in vacuo. 1.7 g of ketone (XX) was obtained with b. p. 97° at 4 mm, n_D^{18} 1.4638. The semicarbazone melted at 173-174°.

SUMMARY

1. It has been shown that depending on the temperature the condensation of bivinyl with trans-crotonaldehyde yields the trans- and cis-forms of Δ^3-tetrahydrotolualdehyde (I) and (II), which undergo reversible thermal isomerization.

2. Under the influence of acids, the cis-aldelyde (II) is isomerized, forming an equilibrium mixture of the cis- and trans-forms of Δ^3-tetrahydrotolualdehyde in the ratio 1 : 3.

3. The condensation of the cis-aldehyde (II) with acetone yields the product of crotonic condensation (XVII), but under similar conditions the condensation of the trans-aldehyde (I) with acetone yields the product of aldol condensation (XVI).

LITERATURE CITED

[1] Diels and Alder, Lieb. Ann. 470, 62 (1929).

[2] Diels and W. Vogt, Lieb. Ann. 564, 120 (1949).

[3] Wichterle, Collection. Czekoslov. Chem. Comun. 10, 497 (1938).

[4] N. B. Henbest, J. Chem. Soc. 1949, 740.

Received October 1, 1956

Institute of Chemistry
and Chemical Technology of the Academy
of Sciences, Lithuanian SSR

ETHYLENE SULFIDE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS WITH TWO HETERO-ATOMS

III. 3-ARYLTHIAZOLIDONES-2 FROM N-(β-MERCAPTOETHYL)ARYLAMINES

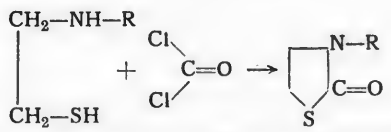
Yu. K. Yuryev and S. V. Dyatlovitskaya

In our previous communications [1, 2] we have shown the possibility of using N-(β-mercaptoethyl)arylamines (easily prepared from ethylene sulfide and arylamines) in condensation with aldehydes to prepare 2-alkyl- (or 2-aryl)-3-arylthiazolidines.

The high reactivity of N-(β-mercaptoethyl)arylamines because of the presence in them of two active hydrogen atoms – in the sulfhydryl and the substituted amine groups – should make it possible to easily carry out condensation reactions with compounds that contain labile halogen atoms, for example with acid chlorides of dibasic acids. In the simplest case of this type of reaction – the condensation of N-(β-mercaptoethyl)arylamines with the acid chloride of carbonic acid – the reaction products should be 3-arylthiazolidones-2.

According to the data in the literature, 3-arylthiazolidones-2 are prepared: a) from 3-arylthiazolidinethiones-2 by replacement of a sulfur atom by oxygen, which is accomplished by the action of mercuric oxide [3], the action of dilute nitric acid or chromic mixture [4], and also by the addition of methyl iodide or monochloroacetic acid with subsequent hydrolysis of the reaction products by silver hydroxide [4-7]; b) from 3-arylthiazolidinimines-2 by hydrolysis with dilute acid [4, 5, 7-9]. However, with these methods it is possible to obtain the 3-arylthiazolidones-2 only in low yields.

In the present work we have carried out the condensation of N-(β-mercaptoethyl)arylamines with phosgene and have prepared a series of 3-arylthiazolidones-2 with yields of 50-90%.



(R = C_6H_5, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$, o-$CH_3OC_6H_4$, p-$CH_3OC_6H_4$, p-$COOC_2H_5C_6H_4$, α-$C_{10}H_7$)

Of the arylated β-aminomercaptans used by us, N-(β-mercaptoethyl)-o-toluidine entered into the condensation with phosgene the least vigorously. Similar behavior of some other ortho-substituted N-(β-hydroxyethyl)- and N-(β-mercaptoethyl)arylamines has occurred in condensations with aldehydes, for example in the preparation of 2-phenyl-3-o-tolyloxazolidine from N-(β-hydroxyethyl)-o-toluidine [10] and in an unsuccessful attempt to prepare the corresponding thiazolidine from N-(β-mercaptoethyl)-o-carbomethoxyaniline [2].

EXPERIMENTAL

Hydrochlorides of N-(β-mercaptoethyl)arylamines

A current of dry hydrogen chloride was passed through a solution of 0.5 g of N-(β-mercaptoethyl)arylamine in absolute ether. A precipitate of N-(β-mercaptoethyl)arylamine hydrochloride separated, which was recrystallized from anhydrous alcohol.

N-(β-mercaptoethyl)aniline hydrochloride: m. p. 125-125.5°.

Found %: N 7.33, 7.73. $C_8H_{12}NSCl$. Calculated %: N 7.38.

N-(β-mercaptoethyl)-p-toluidine hydrochloride: m. p. 184.5-185.5°.

Found %: N 6.96, 7.11. $C_9H_{14}NSCl$. Calculated %: N 6.88.

N-(β-mercaptoethyl)-o-toluidine hydrochloride: m. p. 204-205° (with decomp.).

Found %: N 7.14, 7.32. $C_9H_{14}NSCl$. Calculated %: N 6.88.

N-(β-mercaptoethyl)-p-anisidine hydrochloride: m. p. 152.5-153.5°.

Found %: N 6.80, 6.58. $C_9H_{14}ONSCl$. Calculated %: N 6.38.

N-(β-mercaptoethyl)-o-anisidine hydrochloride: m. p. 158.5-159.5°.

Found %: N 6.51, 6.62. $C_9H_{14}ONSCl$. Calculated %: N 6.38.

N-(β-mercaptoethyl)-α-naphthylamine hydrochloride:* m. p. 184.5-185.5°.

Found %: N 6.15, 6.19. $C_{12}H_{14}NSCl$. Calculated %: N 5.84.

Preparation of 3-arylthiazolidones-2

Method of synthesis. 0.01 g-mole of N-(β-mercaptoethyl)arylamine in 5 ml of toluene was mixed with 7.5 ml of 20% solution of phosgene (0.015 g-mole) in toluene. The reaction started immediately with the evolution of heat. In 2-3 minutes after the beginning of the reaction, precipitation of colorless crystals occurred. After the reaction mixture was cooled, the crystalline precipitate, which was the hydrochloride of the starting N-(β-mercaptoethyl)arylamine, was filtered off, washed twice with toluene (which was then added to the filtrate), and dried. From the combined filtrates, which contained the reaction product, the toluene was distilled off, after which the residue crystallized upon cooling. The crystals obtained were dissolved in alcohol, the solution was decolorized by boiling with activated carbon, filtered, diluted with an equal volume of water, and cooled; colorless crystals of 3-arylthiazolidone-2 precipitated.

3-Phenylthiazolidone-2. To 1.53 g of N-(β-mercaptoethyl)aniline in 5 ml of toluene was added 7.5 ml of a 20% solution of phosgene in toluene. 0.35 g of crystals was separated, which melted at 125-125.5° (from alcohol) and was the hydrochloride of N-(β-mercaptoethyl)aniline: a mixed sample with crystals of known N-(β-mercaptoethyl)aniline hydrochloride gave no depression. From the filtrate was obtained 1.45 g (81%) of 3-phenylthiazolidone-2: m. p. 76.5-77.5° (from 50% alcohol).

Found %: C 60.37, 60.34; H 5.23, 5.20; N 7.90, 7.79. C_9H_9ONS. Calculated %: C 60.31; H 5.06; N 7.81.

Literature data for 3-phenylthiazolidone-2 [4]: m. p. 79°.

3-p-Tolylthiazolidone-2. 1.67 g of N-(β-mercaptoethyl)-p-toluidine in 5 ml of toluene was mixed with 7.5 ml of a 20% solution of phosgene in toluene. 0.12 g of crystals was separated, which melted at 184.5-185.5° (from alcohol) and was the hydrochloride of N-(β-mercaptoethyl)-p-toluidine: a mixed sample with crystals of known N-(β-mercaptoethyl)-p-toluidine hydrochloride gave no depression. From the filtrate was obtained 0.82 g (85%) of crystals of 3-p-tolylthiazolidone-2: m. p. 93-93.5° (from 50% alcohol).

Found %: C 62.32, 62.35; H 6.00, 5.95; N 7.37, 7.33. $C_{10}H_{11}ONS$. Calculated %: C 62.14; H 5.67; N 7.25.

Literature data for 3-p-tolylthiazolidone-2 [5]: m. p. 88°.

3-o-Tolylthiazolidone-2. To 1.67 g of N-(β-mercaptoethyl)-o-toluidine in 5 ml of toluene was added 7.5 ml of a 20% solution of phosgene in toluene. 0.92 g of crystals was separated, which melted at 204-205° (with decomp.) and was the hydrochloride of N-(β-mercaptoethyl)-o-toluidine; a mixed sample with crystals of known N-(β-mercaptoethyl)-o-toluidine hydrochloride gave no depression.

* N-(β-mercaptoethyl)-α-naphthylamine, prepared by the usual method [11] of the reaction of ethylene sulfide with α-naphthylamine, was a colorless, thick oil with the following constants: b. p. 175.5-176° (2 mm), n_D^{20} 1.6744, d_4^{20} 1.1566.

From the filtrate was obtained 0.95 g (49%) of 3-o-tolylthiazolidone-2: m. p. 61-62° (from alcohol).

Found %: C 62.30, 62.17; H 5.80, 5.89; N 7.70, 7.49. $C_{10}H_{11}ONS$. Calculated %: C 62.14; H 5.67; N 7.25.

Addition to the reaction mixture of a small amount of trimethylamine or passing a current of air into it did not cause any increase in the yield of the reaction product.

3-p-Anisylthiazolidone-2. To 1.83 g of N-(β-mercaptoethyl)-p-anisidine in 5 ml of toluene was added 7.5 ml of a 20% solution of phosgene in toluene. 0.3 g of crystals was separated, which melted at 152.5-153.5° (from alcohol) and was the hydrochloride of N-(β-mercaptoethyl)-p-anisidine; a mixed sample with known N-(β-mercaptoethyl)-p-anisidine hydrochloride gave no depression.

From the filtrate was obtained 1.8 g (86%) of 3-p-anisylthiazolidone-2: m. p. 102-103° (from alcohol).

Found %: C 57.17, 57.19; H 5.36, 5.41; N 6.98, 6.97. $C_{10}H_{11}O_2NS$. Calculated %: C 57.39; H 5.30; N 6.69.
Literature data for 3-p-anisylthiazolidone-2 [3]: m. p. 102-103°.

3-o-Anisylthiazolidone-2. To 1.83 g of N-(β-mercaptoethyl)-o-anisidine in 5 ml of toluene was added 7.5 ml of a 20% solution of phosgene in toluene. 0.2 g of crystals was separated, which melted at 158.5-159.5° (from alcohol) and was the hydrochloride of N-(β-mercaptoethyl)-o-anisidine; a mixed sample with crystals of known N-(β-mercaptoethyl)-o-anisidine hydrochloride gave no depression.

From the filtrate was obtained 1.90 g (91%) of 3-o-anisylthiazolidone-2: m. p. 116.5-117° (from alcohol).

Found %: C 57.31, 57.13; H 5.43, 5.51; N 6.74, 6.91. $C_{10}H_{11}O_2NS$. Calculated %: C 57.39; H 5.30; N 6.69.
Literature data for 3-o-anisylthiazolidone-2 [6]: m. p. 116°.

3-α-Naphthylthiazolidone-2. 2.03 g of N-(β-mercaptoethyl)-α-naphthylamine in 5 ml of toluene was mixed with 7.5 ml of a 20% solution of phosgene in toluene. 0.24 g of crystals was separated, which melted at 184.5-185° (from alcohol) and was the hydrochloride of N-(β-mercaptoethyl)-α-naphthylamine; a mixed sample with crystals of known N-(β-mercaptoethyl)-α-naphthylamine hydrochloride gave no depression. From the filtrate was obtained 2.05 g (90%) of 3-α-naphthylthiazolidone-2: m. p. 142.5-143° (from alcohol).

Found %: C 68.11, 68.15; H 4.87, 4.88 ; N 6.45, 6.26. $C_{13}H_{11}ONS$. Calculated %: C 68.07; H 4.83; N 6.11.
Literature data for 3-α-naphthylthiazolidone-2 [7]: m. p. 102°.

3-p-Carboethoxyphenylthiazolidone-2. 1.12 g of N-(β-mercaptoethyl)-p-carboethoxyaniline in 2.5 ml of toluene was mixed with 3.75 ml of a 20% solution of phosgene in toluene. The precipitate that separated (0.1 g), which did not contain sulfur, was soluble in water, and formed a gelatinous mass with alcohol, and was not investigated further. From the filtrate was obtained 0.92 g (74%) of 3-p-carboethoxyphenylthiazolidone-2: m. p. 107-108° (from alcohol).

Found %: C 57.65, 57.75; H 5.21, 5.28; N 5.86, 5.88. $C_{12}H_{13}O_3NS$. Calculated %: C 57.35; H 5.21; N 5.57.

3-p-Carboethoxyphenylthiazolidone-2 was soluble in ether, acetone, benzene, dichloroethane; slightly soluble in alcohol; insoluble in water.

SUMMARY

The condensation of N-(β-mercaptoethyl)arylamines with phosgene, which takes place readily, is a convenient method for the preparation of 3-arylthiazolidones-2. By this method we obtained 3-phenyl-, 3-p-tolyl-, 3-p-anisyl-, 3-o-anisyl-, and 3-α-naphthylthiazolidones-2 and also 3-o-tolyl- and 3-p-carboethoxyphenylthiazolidones-2, which had not been described in the literature. Along with the 3-arylthiazolidones-2 a small amount was produced of the hydrochlorides of the starting N-(β-mercaptoethyl)-arylamines.

LITERATURE CITED

[1] Yu. K. Yuryev and L. S. German, J. Gen. Chem. 26, 550 (1956).*

[2] Yu. K. Yuryev and S. V. Dyatlovitskaya, J. Gen. Chem. 27, 1787 (1957).*

* Original Russian pagination. See C. B. Translation.

[3] H. Erlenmeyer, H. Schulthess, H. Bloch, Helv. Chim. Acta. 30, 1336 (1947).

[4] W. Will, Ber. 15, 338 (1882).

[5] W. Will, O. Bielschowski, Ber. 15, 1309 (1882).

[6] F. Förster, Ber. 21, 1865 (1888).

[7] F. Evers, Ber. 21, 962 (1888).

[8] G. Raiziss, W. Clemence, J. Am. Chem. Soc. 63, 3124 (1941).

[9] Hunter, H. Kolloff, J. Am. Chem. Soc. 65, 156 (1943).

[10] Yu. K. Yuryev, L. F. Gorin and A. N. Vysokosov, J. Gen. Chem. 24, 1851 (1954).*

[11] Yu. K. Yuryev and L. S. German, Messenger Moscow State Univ., No. 1, 197 (1956).

Received October 1, 1956

Moscow State University

*Original Russian pagination. See C. B. Translation.

INVESTIGATION IN THE FIELD OF THE SYNTHESIS OF ORGANOSILICON COMPOUNDS

III. STUDY OF THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES

A. L. Klebansky and V. S. Fikhtengolts

The direct reaction of alkyl chlorides with silicon in the presence of copper as a catalyst has been characterized by Rochow as universal. Using a contact mass of elemental silicon and copper he prepared several alkylchloro- and bromosilanes [1]. With this same contact mass at 250°, the following allylchlorosilanes have been synthesized: $C_3H_5SiHCl_2$, $C_3H_5SiCl_3$, and $(C_3H_5)_2SiCl_2$ [2]. An attempt to synthesize directly vinylchlorosilanes gave only negligible yields of these compounds [2]. This contact mass proved to be useless for the preparation of phenylchlorosilanes. Substitution of silver for the copper or oxidation of an alloy of silicon and copper in a stream of air at 300° for 15 hours made possible the preparation of some diphenyldichlorosilane and phenyltrichlorosilane [3]. Passing ethers and HCl over silicon in the presence of copper also has been recommended for the preparation alkylchlorosilanes [4]. It has proved possible to synthesize directly even esters of orthosilicic acid [5]. Thus, when vapors of methyl alcohol at 250° or ethyl alcohol at 280-325° are passed over a contact mass of silicon and copper, a reaction occurs with the formation of tetraalkoxysilanes.

Thus, the direct synthetic reaction proposed by Rochow [1] theoretically appears to be general for the preparation of a series of different organosilicon compounds, but from the practical point of view the universality of this reactions is very limited. According to our experimental data, presented in Table 1, as the organic radical of the alkyl chloride becomes larger and more complex, the amount of hydrogen-containing compounds of the type $RSiHCl_2$ and $HSiCl_3$ in the reaction products increases. The amount of the compound R_2SiCl_2, which is of practical value, sharply decreases down to zero.

The explanation of this is to be sought, apparently, in the fact that with an increase in the size of the organic radical its thermal stability decreases. Consequently, along with the dissociation of the alkyl chloride at the C—Cl bond, which leads to the formation of the alkylchlorosilanes, there occurs, even in spite of lowering the reaction temperature, a purely thermal decomposition with the formation of HCl, atomic hydrogen, and unsaturated compounds. As a result of this there also is observed an increase in the amount of $HSiCl_3$ and $RSiHCl_2$ in the reaction products. Thus, this method of synthesis is useful for the preparation of products of practical value of the type R_2SiCl_2 only in the case of alkyl chlorides of sufficient thermal stability, such as CH_3Cl and C_2H_5Cl.

The relation between the temperature of the process and the yields of the main product and the by-products of the reaction has been noted in previous communications [6, 7] and has been indicated in the mechanism proposed by us for the process. These data permit us to assume that the temperature of the reaction zone is the chief factor, which in considerable degree determines the yields and the composition of the reaction products.

As has been shown by experimental study, an increase in the temperature of the reaction zone brings about an increase in the degree of conversion of methyl chloride, but the yield of dimethyldichlorosilane decreases. At the same time the yield of gaseous decomposition products of methyl chloride increases (Fig. 1). The methyltrichlorosilane content of the condensate simultaneously increases. The similar course of the curves for the CH_3SiCl content of the condensate and for the decomposition of the CH_3Cl with an increase in temperature again confirms the conception that has been stated concerning the reaction mechanism with regard to the existence of a relation between the processes of formation of methyltrichlorosilane and thermal decomposition of methyl chloride. Numerous further observations have shown that when the temperature is increased, the changes in the amount of gaseous products formed and the amount of carbon deposited on the contact mass always correspond with the changes in the yields of methyltrichlorosilane (Table 2).

TABLE 1

Products of Direct Synthesis Reaction with Certain Alkyl Chlorides

Alkyl chloride	Reaction temperature	Composition of reaction products (in %)			
		$HSiCl_3$	$RSiHCl_2$	$RSiCl_3$	R_2SiCl_2
CH_3Cl	280—300°	—	5	35	50
CH_3CH_2Cl	190	—	51	7	34
$CH_2=CHCl$	220	15	45.5	25	15
$CH_3CH_2CH_2Cl$ . . .	170	7	82.5	11	—
$(CH_3)_2CHCl$	150	34	66	—	—

TABLE 2

Correlation Between Yields of CH_3SiCl_3 and Decomposition of CH_3Cl

Temperature of experiment	Yield of CH_3SiCl_3 based on CH_3Cl (in %)	Degree of decomp. of CH_3Cl (in %)	
		from amount of carbon deposited on contact mass	from data of gas analysis
350°	19.5	18	26.5
370	23	24	28
370	24	25.5	27
400	29	31.5	39

TABLE 3

Effect of Temperature of Experiment in Synthesis of Ethylchlorosilanes

Temperature of expt.	Degree of conversion of C_2H_5Cl (%)	Content of condensate (%)			Degree of decomp. of C_2H_5Cl (in % of reacted material)	Content of gas (in %)			
		$C_2H_5SiHCl_2$	$C_2H_5SiCl_3$	$(C_2H_5)_2SiCl_2$		H_2	$CH_2=CH_2$	CH_4	C_2H_6
190°	73	50.8	6.6	33.8	25	18	76	6	—
250	100	33.6	21.5	29.1	30	22	69	7.6	1.4

A similar picture of the change in composition of the condensate upon raising the temperature of the reaction zone is observed for the synthesis of the ethylchlorosilanes by the same method (Table 3). Here also when the temperature of the reaction zone is raised, a lowering in the yield of diethyldichlorosilane and an increase in the yields of ethyltrichlorosilane are observed. Simultaneously the degree of conversion of the ethyl chloride and its pyrolysis increase.

Along with the temperature factor, other kinetic factors also exert a known influence on the course of the process, such as the time of contact and the pressure, for example. Consideration of their effect also is of interest from the point of view of explaining the mechanism of the process. One of the most important parameters of contact-catalytic reactions is the duration of juxtaposition of the reacting materials with the catalyst; however, the reaction of methyl chloride with silicon that we have studied has a number of peculiarities in comparison with the usual contact-catalytic processes. Consequently the time of contact between the methyl chloride and the silicon has comparatively little effect on the yields of the reaction products.

TABLE 4

Effect of Addition of CH_3SiCl_3 on Yield of Reaction Products

Composition of starting mixture (in %)			Temperature, beginning of reaction	Degree of decomposition of CH_3Cl (in % of material reacted)	Yield based on CH_3Cl reacted (in %)	
CH_3Cl	N_2	CH_3SiCl_3			CH_3SiCl_3	$(CH_3)_2SiCl_2$
77	23	—	275°	20	39	31
80	—	20	275	16.5	31.5	33
59	41	—	310	26	36	29
47	—	53	310	14	26.5	28

TABLE 5

Pressure (atm)	Temp., beginning of reaction	Contact time, (sec)	Degree of conversion of CH_3Cl (in %)	Yield of condensate from 100 g contact mass	Degree of decomp. of CH_3Cl (in % of reacted material)	Yield based on CH_3Cl reacted (in %)		Content of condensate (%)	
						CH_3SiCl_3	$(CH_3)_2SiCl_2$	CH_3SiCl_3	$(CH_3)_2SiCl_2$
0	300°	32	91.5	8.7	22	40	28	42.5	38
4	240	27	68	40.7	6	30.5	41	29.5	50.5
8	235	40	61	46.6	8.5	26.5	40	27	53.5
12	230	73	84.5	50.1	14	29	39	30	52.5

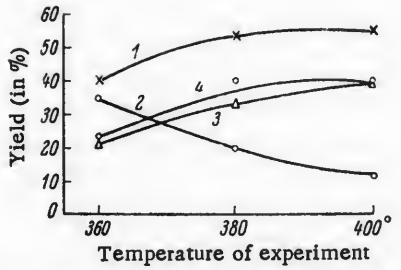


Fig. 1. Effect of temperature of reaction. 1) Degree of conversion of CH_3Cl; 2) $(CH_3)_2SiCl_2$ content of condensate; 3) degree of decomposition of CH_3Cl (in % of material reacted); 4) CH_3SiCl_3 content of condensate.

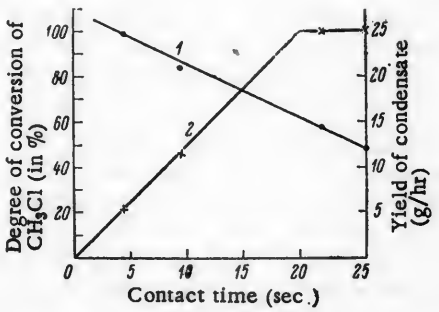


Fig. 2. Effect of contact time. 1) Yield of condensate from 100 g of contact mass; 2) degree of conversion of methyl chloride.

The data obtained (Fig. 2) show that an increase in the contact time gives rise to an increase in the degree of conversion of the methyl chloride, but the quantitative yield of the condensate in unit time falls in relation to a decrease in the amount of methyl chloride submitted to reaction. The composition and comparative yields of the reaction products are almost unchanged (Fig. 3).

The latter fact permits the assumption that the reactions producing CH_3SiCl_3 and $(CH_3)_2SiCl_2$ are not interdependent. In order to verify this circumstance a series of experiments was set up in which dimethyldichlorosilane

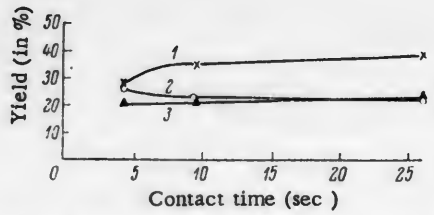


Fig. 3. Effect of contact time.
1) Yield of $(CH_3)_2SiCl_2$; 2) yield of CH_3SiCl_3; 3) degree of decomposition of CH_3Cl (in % of material reacted).

(alone and in mixture with H_2, with HCl, and with CH_3Cl), and also methyltrichlorosilane, was passed over copper at 350-400°. In no case were any changes observed in the methylchlorosilanes in question. This is evidence of the thermal and chemical stability of the compounds under the conditions of synthesis of the methylchlorosilanes. The absence of any sequence in the reactions producing $(CH_3)_2SiCl_2$ and CH_3SiCl_3 is also confirmed by the fact that when the synthesis of the methylchlorosilanes was carried out with the addition to the methyl chloride of CH_3SiCl_3 in vapor form, the yield of the latter was reduced while the yield of $(CH_3)_2SiCl_2$ remained unchanged (Table 4).

Similarly the yield of $(CH_3)_2SiCl_2$ remained constant in synthesis in the presence of HCl and Mg, where there was considerable change in the yields of CH_3SiCl_3 [6].

The effect of increasing the pressure was of interest from the point of view of confirming the proposed mechanism of the process. According to the radical mechanism of Hurd and Rochow [8], the reaction of direct synthesis should take place at a higher temperature under pressure, since pressure, as is well known, hinders the breaking up of molecules to form free radicals. On the other hand, according to the chemosorption mechanism proposed by us for the process, a lowering of the reaction temperature would be expected, since pressure promotes the adsorption of molecules of methyl chloride on the contact mass. The experimental data (Table 5) show that when the pressure is increased the starting temperature of the reaction is lowered by 60-70°.

Corresponding with a lowering of the temperature there is observed a decrease in the degree of conversion of the methyl chloride, a considerable decrease in its decomposition, and, as a consequence of the latter, a decrease in the yield of methyltrichlorosilane. The yield of dimethyldichlorosilane correspondingly increases and the composition of the condensate is improved.

Raising the pressure increases to a marked degree of quantitative yield of the condensate in unit time; however, this increase in efficiency is not proportional to the increase in pressure: the greatest increase in yield is observed when the pressure is increased from 0 to 4 atm; upon further rise in pressure the increase in yield from the process is slower and slower. This also is explained from the viewpoint of a chemosorption mechanism for the process. A rise in pressure favors the surface adsorption of methyl chloride on the active centers of the contact mass, which also is apparent in the increase in quantitative yield of the reaction products. However, as the pressure increases, a smaller and smaller part of the active surface remains free, and in connection with this the increase in efficiency of the process slows down with further rise in pressure.

An attempt to increase the yield of the process still more by shortening the contact time to 8-10 seconds at 4-8 atm pressure led to a sharp deterioration in the course of the process as a result of the impossibility of a sufficiently rapid removal of the heat produced by the violent reaction. The reaction, which started even at 200-210°, accelerated so much in 3-5 minutes that the temperature in the apparatus rose to 300-305° and the experiment had to be stopped. In this experiment there was observed an extremely vigorous decomposition of methyl chloride and the evolution of large volumes of gas, as a result of which the dimethyldichlorosilane content of the condensate fell to 25-27%, and the methyltrichlorosilane content rose to 50%.

Thus, the use of high pressure (4-5 atm) in the synthesis of methylchlorosilanes is expedient both from the point of view of increasing the efficiency of the process and from the point of view of raising the yield of dimethyldichlorosilane owing to the further lowering of the reaction temperature.

SUMMARY

1. The conditions for carrying out the synthesis of methylchlorosilanes have been studied and the factors have been established which influence the yield of dimethyldichlorosilane and the efficiency of the process.

2. It has been shown that an increase in the temperature of the reaction area promotes thermal decomposition of the methyl radicals, as a result of which the yield of methyltrichlorosilane and the decomposition products of methyl chloride are increased and the yield of dimethyldichlorosilane is decreased.

3. When the contact time is decreased, the degree of conversion of methyl chloride is lowered and the quantitative yield of condensate per unit time is increased. The composition of the reaction products is almost unchanged.

4. It has been established that when the synthesis of the methylchlorosilanes is carried out under pressure (4-12 atm) the reaction temperature is lowered, as a result of which the conditions for conducting the process are improved. The optimum pressure is 4-5 atm.

5. It has been shown that the formation of $(CH_3)_2SiCl_2$ is a process parallel to the reaction producing CH_3SiCl_3.

6. The data obtained are in good agreement with the chemosorption mechanism proposed previously for the reaction, which is additional confirmation of the hypothesis.

LITERATURE CITED

[1] E. G. Rochow, J. Am. Chem. Soc. 67, 963 (1945).

[2] D. T. Hurd, J. Am. Chem. Soc. 67, 1813 (1945).

[3] E. G. Rochow, W. F. Gilliam, J. Am. Chem. Soc. 67, 1772 (1945).

[4] E. G. Rochow, U. S. Patent No. 2459539; Ch. A. 1949, 3025.

[5] E. G. Rochow, J. Am. Chem. Soc. 70, 2171 (1948).

[6] A. L. Klebansky and V. S. Fikhtengolts, J. Gen. Chem. 26, 2502 (1956). *

[7] V. S. Fikhtengolts and A. L. Klebansky, J. Gen. Chem. 27, 2475 (1957).*

[8] D. T. Hurd, E. G. Rochow, J. Am. Chem. Soc. 67, 1057 (1945).

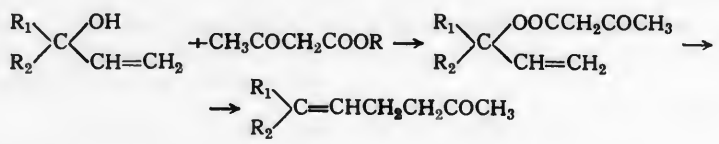
Received August 29, 1956

* Original Russian pagination. See C. B. Translation.

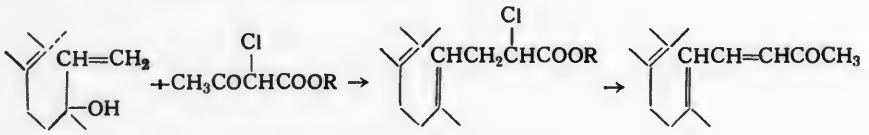
NEW METHODS OF SYNTHESIS FOR THE ESTERS OF POLYENE CARBOXYLIC ACIDS. I.

I. K. Saricheva, G. A. Vorobyeva and N. A. Preobrazhensky

One of the most successful means of obtaining polyene ketones, particularly pseudoionone and pseudoirone, is the synthesis from the β,γ-unsaturated alcohol and acetoacetic ester or diketene, a method which has recently received considerable attention in the literature. The conversion of linalool into geranylacetone with the aid of acetoacetic ester was described in 1940. The reaction has also been carried out with other alkenic alcohols [1]. In 1943 a paper appeared on the synthesis of similar compounds by heating substituted allyl acetoacetates, obtained from the corresponding alcohols and diketene [2]. It was stated as a hypothesis, soon to be completely confirmed, that, in this and the similar reaction with acetoacetic ester, the formation of ketones from alcohols goes through the stage of an ester of acetoacetic acid, which relatively easily undergoes intramolecular rearrangement with simultaneous decarboxylation [3].

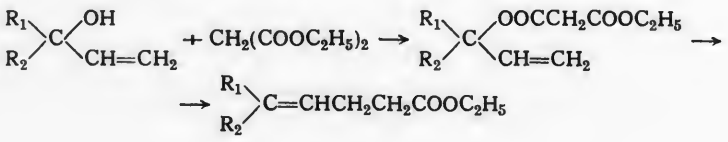


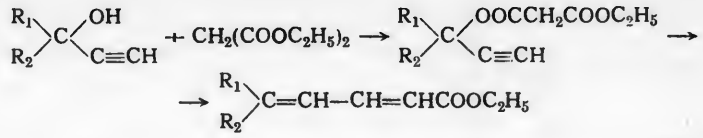
In order to synthesize ketones with conjugated double bonds it was proposed in 1950 in the case of pseudoirone to use the chlorine substituted derivative instead of acetoacetic ester. In this case a necessary stage was the dehydrochlorination of the chloroketone intermediate [4].



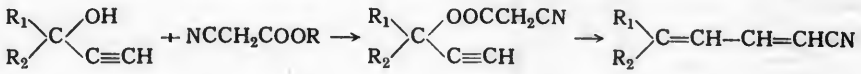
Subsequently, simpler means were found for obtaining conjugated diene systems starting from acetylenic alcohols and diketene [5], acetoacetic ester or its homologs [6].

The investigation of these transformations showed the possibility of obtaining unsaturated compounds with carbethoxy groups from substituted ethylenic or acetylenic alcohols and malonic ester, via an intermediate carbethoxyacetate.

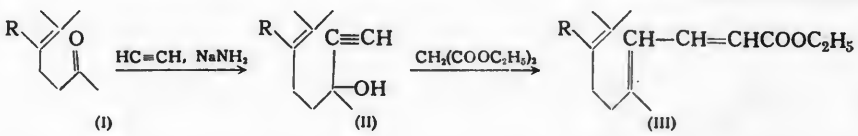




The reaction of a β,γ-unsaturated alcohol with cyanoacetic ester was used to synthesize the nitrile via the cyanoacetate.



By condensing malonic ester with 2,3,6-trimethyl-2-octen-7-yn-6-ol (II, R = CH_3) and 2,6-dimethyl-2-octen-7-yn-6-ol (II, R = H), obtained from 2,3-dimethyl- (I, R = CH_3) and 2-methyl-2-hepten-6-one (I, R = H) and acetylene [7], it was possible to synthesize the ethyl esters of 2,3,6-trimethyl-2,6,8-decatrien-10-oic acid (III, R = CH_3) (yield 30%) and 1,6-dimethyl-2,6,8-decatrien-10-oic acid (III, R = H) (yield 38%).



The structures of the esters (III, R = CH_3 and R = H) were confirmed by determining their physico-chemical constants and also by their ultraviolet (Fig. 1) and infrared (Fig. 2 and 3) absorption spectra.* The existence of an absorption maximum at 277 mμ in the ultraviolet (Fig. 1) and at 1588 cm^{-1} in the infrared (Fig. 2 and 3) showed the presence of a conjugated system of double bonds in these compounds. Thus starting from 2-methyl-2-hepten-6-one (I, R = H) or its homolog (I, R = CH_3), proceeding via the corresponding β,γ-acetylenic alcohols (II, R = H and R = CH_3), there were obtained the ethyl esters of 2,6-dimethyl-2,6,8-decatrien-10-oic acid (III, R = H) and 2,3,6-trimethyl-2,6,8-decatrien-10-oic acid (III, R = CH_3), containing conjugated systems of double bonds. The reactions developed are general methods of lengthening hydrocarbon chains with simultaneous introduction of an ester group. The ester III (R = CH_3) was also obtained by the Reformatsky reaction between 2,3-dimethyl-2-hepten-6-one (I, R = CH_3) and γ-bromocrotonic ester [8]. For this a necessary stage was the elimination of water from 2,3,6-trimethyl-2,8-decadien-6-ol-10-oic acid (IV) with phosphorus oxychloride or phosphorus tribromide in a pyridine medium. Investigation of the dehydration products showed that this reaction did not give a single product and that, unlike our method of preparation, the ethyl ester of 2,3,6-trimethyl-2,6,8-decatrien-10-oic acid (III, R = CH_3) formed was accompanied by the ethyl ester of 2,3,6-trimethyl-2,5,8-decatrien-10-oic acid (V).

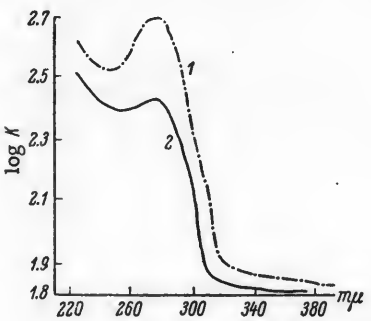


Fig. 1. Ultraviolet spectra. 1) III, R = H; 2) (III, R = CH_3).

* The ultraviolet absorption spectra were obtained with an SF-4 spectrophotometer, using a 1 cm cell. The infrared spectra were obtained with an IKS-11 spectrophotometer (single beam model), using a sodium chloride prism. The source of radiation was a Nernst filament.

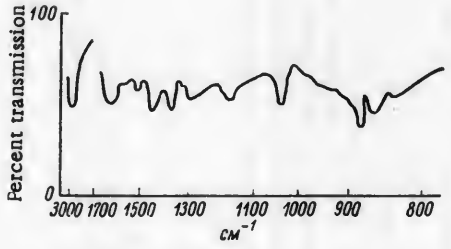


Fig. 2. Infrared spectrum (III, R = CH_3).

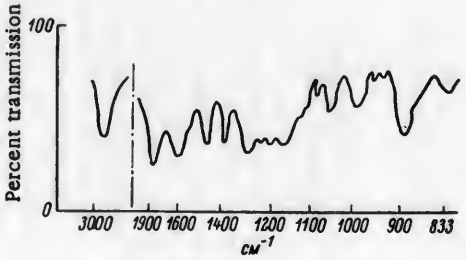


Fig. 3. Infrared spectrum (III, R = H).

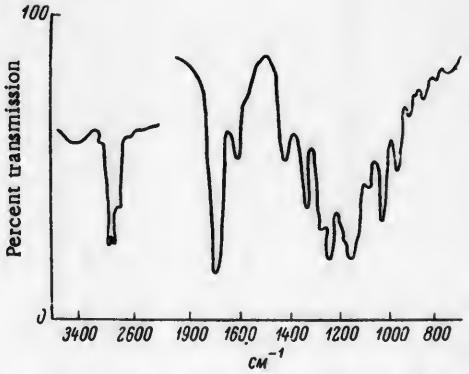


Fig. 4. Infrared spectrum of the ester (1st fraction) obtained by dehydration with $POCl_3$.

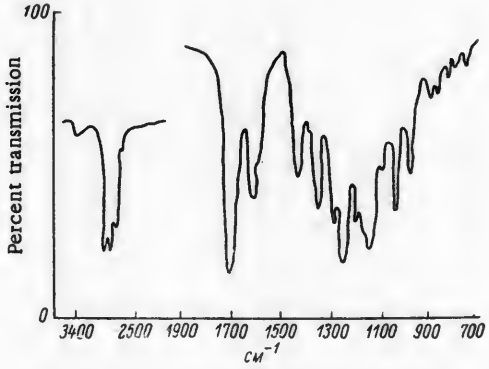


Fig. 5. Infrared spectrum of the ester (2nd fraction) obtained by dehydration with $POCl_3$.

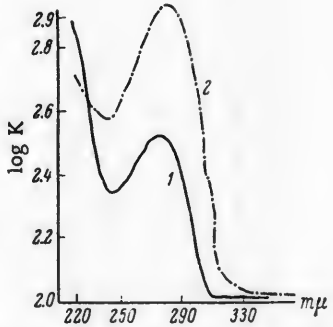


Fig. 6. Ultraviolet spectra of the esters obtained by dehydration with $PoCl_3$.
1) 1st fraction; 2) 2nd fraction.

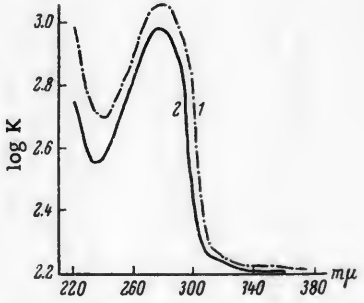
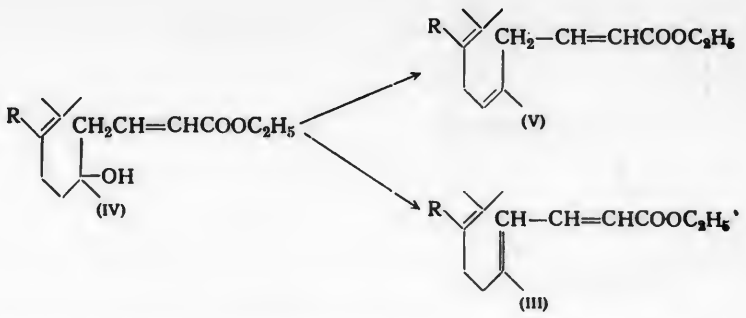


Fig. 7. Ultraviolet spectra of the esters obtained by dehydration with PBr_3.
1) 1st fraction; 2) 2nd fraction.



A comparison of the physico-chemical constants and spectral characteristics (Fig. 4-9) of the products of the Reformatsky reaction indicated that the main component of the first fraction (b.p. 100-102° at 0.4 mm) was

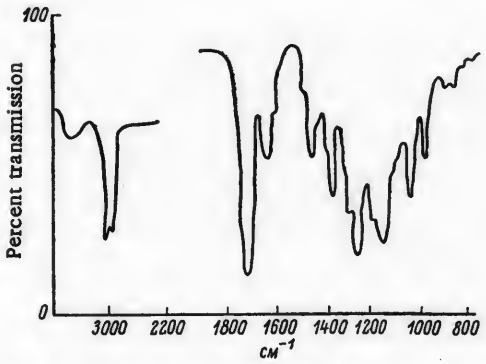


Fig. 8. Infrared spectrum of the ester (1st fraction) obtained by dehydration with PBr_3.

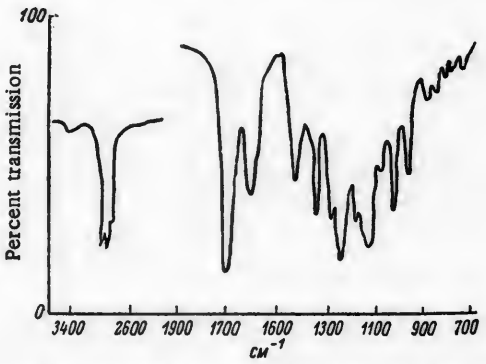


Fig. 9. Infrared spectrum of the ester (2nd fraction) obtained by dehydration with PBr_3.

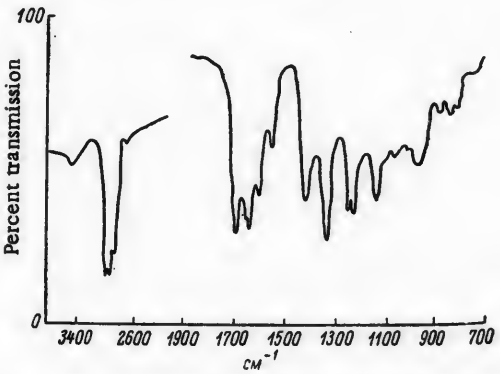


Fig. 10. Infrared spectrum of 2,3,6-trimethyl-2, 5,8-undecatrien-10-one (IX).

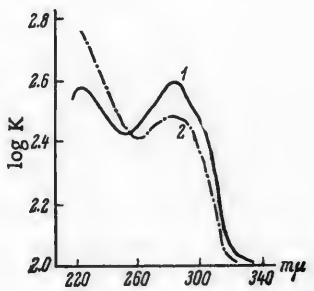
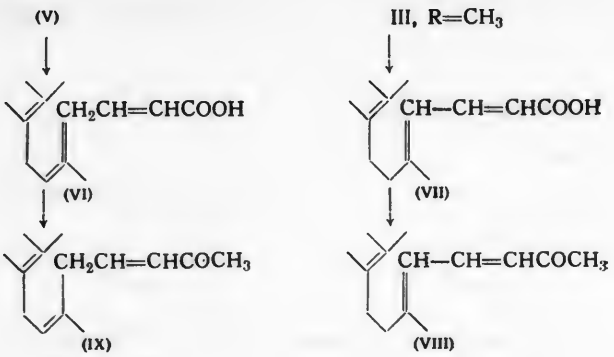


Fig. 11. Ultraviolet spectra. 1) 2,3,6-Trimethyl-2,5,8-undecatrien-10-one (IX). 2) 2,3,6-Trimethyl-2,6,8-undecatrien-10-one.

the ethyl ester of 2,3,6-trimethyl-2,5,8-decatrien-10-oic acid (V). The ester composing the second fraction (b.p. 107-109° at 0.4 mm) had constants and spectra (Fig. 5-7, 9) close to those of the ester III ($R=CH_3$) obtained from 2,3,6-trimethyl-2-octen-7-yn-6-ol (II, $R=CH_3$) and malonic ester. The esters obtained were converted into the corresponding acids (VI, VII) and pseudoirones (VIII and IX), in which a similar arrangement of double bonds was observed (Fig. 10-15).



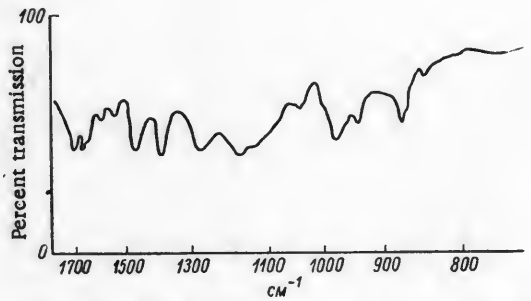


Fig. 12. Infrared spectrum of 2,3,6-trimethyl-2,6,8-undecatrien-10-one (VIII).

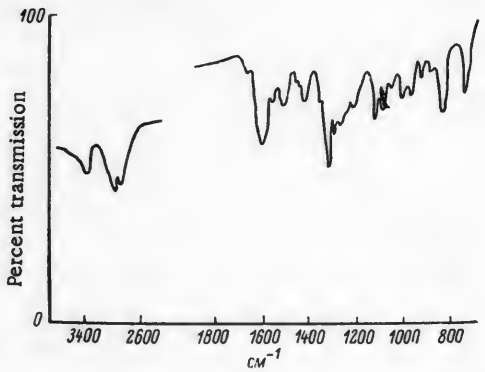


Fig. 13. Infrared spectrum of the 2,4-dinitrophenylhydrazone of the pseudoirone VIII (m.p. 121-122°).

EXPERIMENTAL

1) Ethyl ester of 2,3,6-trimethyl-2,6,8-decatrien-10-oic acid (III, R=CH_3). A mixture of 10 g (0.06 mole) of II (R=CH_3) and 36 g (0.21 mole) of freshly distilled malonic ester was heated in a stream of nitrogen to 180-185° for 55 hours. Evolution of carbon dioxide was observed (detected with barium hydroxide). Excess malonic ester was distilled off at 10 mm, and the residue was redistilled. Yield 4 g (28.15%).

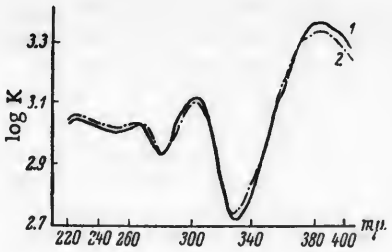


Fig. 14. Ultraviolet spectra of the 2,4-dinitrophenylhydrazones of the pseudoirone VIII. 1) M.p. 121-122°, 2) m.p. 148.5-150°.

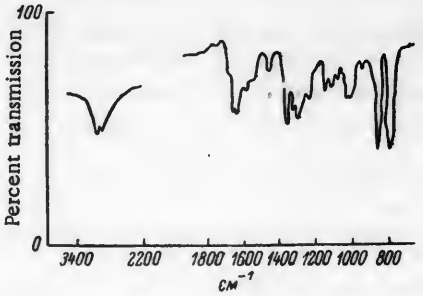


Fig. 15. Infrared spectrum of the 2,4-dinitrophenylhydrazone of the pseudoirone VIII (m.p. 148.5-150°).

B.p. 112-113.5° at 0.6 mm, n_D^{20} 1.5013, d_4^{20} 0.9570, molecular refraction (MR_D) 72.78, calc. for $C_{15}H_{24}O_2$ 71.73.

Found %: C 76.65, H 9.93. $C_{15}H_{24}O_2$ calc. %: C 76.22, H 10.24.

Infrared spectrum – 2899 (v. strong), 1672 (v. strong), 1588 (medium), 1528 (medium, 1453 (v. strong), 1370 (v. strong), 1300 (strong), 1170 (strong), 1042 (v. strong), 880 (strong), 858 (strong) cm^{-1}.

Ultraviolet spectrum – λ_{max} 275 mμ in alcohol (log K 2.43).

2) Ethyl ester of 2,6-dimethyl-2,6,8-decatrien-10-oic acid (III, R=H). A mixture of 30 g (0.197 mole) of II (R=H) and 108 g (0.536 mole) of malonic ester was heated at 170-175° for 50 hours. Unreacted malonic ester was distilled off at 10 mm and the residue was distilled. Yield 15.4 g (35.5%).

B. p. 113-113.5 at 0.7 mm, n_D^{20} 1.5016, d_4^{20} 0.9788 , MR_D 66.99, calc. for $C_{14}H_{22}O_2$ 67.11.

Found %: C 76.05, 75.97; H 9.76, 9.99. $C_{14}H_{22}O_2$ calc. %: C 75.61, H 9.97.

Infrared spectrum – 2857 (v. strong), 1724 (v. strong), 1588 (v. strong), 1530 (weak), 1460 (weak), 1450 (v. strong), 1370 (v. strong), 1282 (strong), 1235 (v. strong), 1212 (v. weak), 1170 (strong), 1124 (v. weak), 1101 (weak), 1042 (strong, 986 (strong), 943 (weak), 900 (strong), 824 (medium) cm^{-1}.

Ultraviolet spectrum – λ_{max} 275 mμ in alcohol (log K 2.7).

3) Ethyl esters of 2,3,6-trimethyl-2,5,8-decatrien-10-oic acid (V) and 2,3,6-trimethyl-2,6,8-decatrien-10-oic acid (III, R=CH_3).

a) Dehydration with phosphorus oxychloride in pyridine. A solution of 27.2 g (0.107 mole) IV in 100 ml of benzene was added with stirring, over a period of 45 minutes, in a current of nitrogen, to a boiling mixture of 21.2 g (0.157 mole) of phosphorus oxychloride, 63.7 g (0.8 mole) of pyridine and 40 ml of benzene. The whole was heated for 1 hour, cooled to room temperature and poured into 100 ml of iced water. The upper benzene layer was separated, washed five times with 30 ml of sulfuric acid (d_4^{20} 1.032), neutralized by washing with aqueous sodium bicarbonate and dried over sodium sulfate. After removal of solvent the residue was distilled.

First fraction – yield 8.6 g (34.03%). B.p. 100-102° at 0.4 mm, 112-115° at 1.5 mm, n_D^{20} 1.4925, d_4^{20} 0.9563 MR_D 71.76. $C_{15}H_{24}O_2$. Calculated 71.72.

Found %: C 76.26, H 9.75. $C_{15}H_{24}O_2$ calc. %: C 76.22, H 10.24.

Infrared spectrum – 2979 (v. strong), 2926 (v. strong), 2860 (v. strong). 1710 (v. strong), 1630 (medium), 1435 (medium), 1350 (strong), 1285 (weak), 1250 (v. strong), 1182 (v. strong), 1090 (weak), 1045 (strong), 990 (medium), 930 (weak), 865 (weak), 740 (weak) cm^{-1}.

Ultraviolet spectrum – λ_{max} 220, 277.5 mμ in alcohol (log K 2.86, 2.52).

Second fraction – Yield 10.2 g (40.36%). B.p. 107-109° at 0.4 mm, 118-120° at 1.5 mm, n_D^{20} 1.4996, d_4^{20} 0.9408, MR_D 73.75, calc. for $C_{15}H_{24}O_2$ 71.72.

Found %: C 75.95, H 9.78; $C_{15}H_{24}O_2$ calc. %C 76.22, H 10.24.

Infrared spectrum – 2978 (v. strong), 2926 (v. strong), 2856 (v. strong), 1700 (v. strong), 1600 (medium), 1413 (medium), 1350 (strong), 1290 (weak), 1240 (v. strong), 1165 (medium), 1130 (v. strong), 1083 (weak), 1020 (medium), 965 (medium), 860 (weak), 840 (weak), 815 (weak), 775 (weak), 750 (weak), 725 (weak) cm^{-1}.

Ultraviolet spectrum – λ_{max} 220, 277.5 mμ in alcohol (log K 2.76, 2.94).

b) Dehydration with phosphorus tribromide in pyridine and petroleum ether. A solution of 11.5 g (0.045 mole) of IV and 10.8 g (0.136 mole) of pyridine in 13 ml of petroleum ether was added drop by drop, with stirring, in a current of nitrogen, to a cold (0°) mixture of 14.25 g (0.053 mole) of phosphorus tribromide, 0.29 g of pyridine and 10 ml of petroleum ether (b. p. 40-70° at 762 mm). After adding 5.9 g (0.075 mole) of pyridine the reaction mixture was allowed to stand for 30 minutes at room temperature, heated to 70° for 15 minutes, cooled to 0° and poured into 100 ml of iced water. The upper layer was separated and the lower layer was extracted with benzene (twice with 100 ml). The combined extracts were washed five times with 20 ml of sulfuric acid (d_4^{20} 1.032), neutralized by washing with aqueous sodium bicarbonate and dried over sodium sulfate. After removal of solvent the residue was distilled.

First fraction – Yield 3.5 g (32.75%). B. p. 107-109° at 0.65 mm, n_D^{20} 1.4926, d_4^{20} 0.9561, MR_D 71.86, calc. for $C_{15}H_{24}O_2$ $\overline{F}_3$ 71.72.

Infrared spectrum – 2979 (v. strong), 2926 (v. strong), 2860 (v. strong), 1695 (v. strong), 1620 (medium), 1435 (medium), 1350 (weak), 1290 (weak), 1250 (v. strong), 1150 (weak), 1130 (v. strong), 1060 (weak), 1015 (strong), 965 (medium), 875 (weak), 840 (weak), 795 (weak), 740 (weak) cm^{-1}.

Ultraviolet spectrum – λ_{max} 220, 277.5 mμ in alcohol (log K 3, 3.06).

Second fraction – Yield 4 g (37.44%). B. p. 108-110° at 0.5 mm, n_D^{20} 1.4999, d_4^{20} 0.9408, MR_D 73.86, calc. for $C_{15}H_{24}O_2$ $\overline{F}_3$ 71.72.

Infrared spectrum – 2978 (v. strong), 2925 (v. strong), 2856 (v. strong), 1700 (v. strong), 1610 (medium), 1435 (medium), 1350 (strong), 1290 (weak), 1250 (v. strong), 1195 (medium), 1140 (strong), 1040 (strong), 970 (weak), 890 (weak), 860 (weak), 790 (weak), 730 (weak) cm^{-1}.

Ultraviolet spectrum – λ_{max} 220, 277.5 mμ in alcohol (log K 2.75, 2.98).

4) 2,3,6-Trimethyl-2,5,8-decatrien-10-oic acid (VI). A mixture of 25.4 ml of 10% alcoholic caustic potash with 6.35 g (0.027 mole) of V was heated to boiling in a stream of dry nitrogen for 2.5 hours. The alcohol was distilled off in vacuo. The residue was dissolved in 20 ml of iced water and extracted with 40 ml of ether. The aqueous solution was acidified with 15 ml of sulfuric acid (d_4^{20} 1.066) and extracted with 100 ml of ether, and the extract was dried over sodium sulfate. After distilling off the solvent the product (4 g) was obtained in the form of a thick yellow mass.

S-benzylpseudothiourea salt of 2,3,6-trimethyl-2,5,8-decatrien-10-oic acid. A solution of 0.6 g of the acid in 5 ml of 96% ethyl alcohol was neutralized with 5% alcoholic caustic soda to a pH 6.5-7, and then treated with a hot solution of 1 g of the chloride of S-benzylpseudothiourea in 5 ml of 96% ethyl alcohol. After cooling to 0°, the crystals formed were filtered off and twice recrystallized from anhydrous ethyl alcohol. M. p. 151.5-152°.

Found %: C 67.74, 67.56, H 7.84, 7.84, N 7.30, 7.25. $C_{21}H_{30}O_2N_2S$, calc. %: C 67.33, H 8.07, N 7.48.

Ultraviolet spectrum – λ_{max} 268, 292 mμ in alcohol (log K 3.07, 3.08).

5) 2,3,6-Trimethyl-2,6,8-decatrien-10-oic acid (VII). A mixture of 30.2 ml of 10% caustic potash with 7.55 g (0.032 mole) of III (R = CH_3) was heated to boiling in a stream of dry nitrogen for 2.5 hours. Alcohol was distilled off at 35 mm pressure, and the residue was dissolved in 25 ml of iced water and extracted three times with 15 ml of ether. The aqueous solution was acidified with 20 ml of sulfuric acid (d_4^{20} 1.066) and extracted with 120 ml of ether, and the extract was dried over sodium sulfate. The solvent was distilled off, and 5.63 g of the product was obtained in the form of a thick dark yellow mass. For identification, this acid was converted into the S-benzylpseudothiourea salt as described above and purified by recrystallization from 10 ml of anhydrous alcohol. M. p. 154-154.6°.

Found %: C 67.07, 67.39, H 7.76, 7.75, N 7.21, 7.28. $C_{21}H_{30}O_2N_2S$, calc. %: C 67.33, H 8.07, N 7.48.

Ultraviolet spectrum – λ_{max} 268, 292 mμ in alcohol (log K 3.34, 3.28).

A mixture of the S-benzylpseudothiourea salts of 2,3,6-trimethyl-decatriene-(2,6,8) acid-(10) (VII) (m. p. 151.5-152°) and 2,3,6-trimethyl-decatriene-(2,5,8) acid-(10) (VI) (m. p. 154-154.6°) melted at 145.7-146.5°.

6) 2,3,6-Trimethyl-2,5,8-undecatrien-10-one, pseudoirone (IX). A solution of 1 g (0.045 mole) of lithium methyl in 40 ml of ether was added, drop by drop, to a solution of 2.7 g (0.013 mole) of VI in 30 ml of ether. The reaction mixture was heated to boiling in a stream of dry nitrogen for 45 minutes. After cooling and adding 30 ml of iced water, the upper layer was separated and the lower layer was extracted with ether. The combined extracts were washed with 20 ml of a saturated aqueous solution of sodium thiosulfate, neutralized with sodium bicarbonate and dried over sodium sulfate. The solvent was removed and the residue was distilled. Yield 1.5 g (56.1%).

B. p. 103-105° at 0.7 mm, n_D^{20} 1.4978, d_4^{20} 0.9200, MR_D 65.70, $C_{14}H_{22}O$ calc. 65.46.

Found %: C 81.41, H 10.48. $C_{14}H_{22}O$ calc. % C 81.49, H 10.75.

Infrared spectrum – 2979 (strong), 2926 (v. strong), 2856 (v. strong), 1700 (v. strong), 1655 (v. strong), 1610 (strong), 1570 (medium), 1435 (strong), 1350 (v. strong), 1260 (strong), 1240 (strong), 1150 (strong), 1080 (weak), 970 (medium), 890 (medium), 845 (medium), 810 (weak) cm^{-1}.

Ultraviolet spectrum – λ_{max} 225, 286 mμ in alcohol (log K 2.57, 2.59).

7) 2,3,6-Trimethyl-2,6,8-undecatrien-10-one, pseudoirone (VIII). The preparation was carried out as above; the quantities used were 6 g (0.028 mole) of VII in 40 ml of ether and 2.5 g (0.114 mole) of lithium methyl in 60 ml of ether. Yield 3.4 g (57.2%).

B. p. 106-108° at 0.7 mm, n_D^{20} 1.5260, d_4^{20} 0.9093, MR_D 69.69, calc. for $C_{14}H_{22}O$ 65.46.

Found %: C 81.1, H 10.55. $C_{14}H_{22}O$, calc. %: C 81.49, H 10.75.

Infrared spectrum – 1700 (strong), 1672 (strong), 1605 (strong), 1453 (v. strong), 1380 (v. strong), 1265 (v. strong), 1163 (v. strong), 1122 (weak), 1042 (medium), 986 (strong), 943 (medium), 880 (strong), 853 (medium) cm^{-1}.

Ultraviolet spectrum – λ_{max} 220, 285 mμ in alcohol (log K 2.78, 2.59).

The 2,4-dinitrophenylhydrazone was purified by recrystallization from a mixture of 15 ml of ethyl alcohol and 10 ml of ethyl acetate. The crystals were bright red in color. M. p. 148.5-150°.

Found %: C 61.95, 62.33, H 6.90, 7.11, N 14.67. $C_{20}H_{26}O_4N_4$. Calc. %: C 62.15, H 6.78, N 14.50.

Infrared spectrum – 2920 (strong), 2820 (strong), 1605 (weak), 1585 (strong), 1535 (weak), 1500 (weak), 1405 (medium), 1305 (v. strong), 1285 (strong), 1250 (v. strong), 1196 (medium), 1110 (medium), 1070 (weak), 1040 (weak), 990 (weak), 965 (weak), 915 (weak), 810 (v. strong), 750 (v. strong) cm^{-1}.

Ultraviolet spectrum – λ_{max} 385 mμ in alcohol (log K 3.345).

The filtrate from this 2,4-dinitrophenylhydrazone of m. p. 148.5-150° was allowed to stand for a day at room temperature; a further crop of orange-red crystals deposited and was recrystallized from a mixture of 10 ml of ethyl alcohol and 5 ml of ethyl acetate. M. p. 121-122°.

Found %: N 14.76, 14.78. $C_{20}H_{26}O_4N_4$, calc. %: N 14.50.

Infrared spectrum – 2920 (strong), 2820 (strong), 1585 (weak), 1495 (weak), 1405 (medium), 1340 (weak), 1305 (v. strong), 1285 (strong), 1250 (medium), 1196 (medium), 1110 (medium), 1070 (medium), 1050 (weak), 990 (weak), 965 (weak), 915 (weak), 870 (weak), 820 (v. strong), 725 (v. strong) cm^{-1}.

Ultraviolet spectrum – λ_{max} 385 mμ in alcohol (log K 3.35).

SUMMARY

1) A new method has been developed by the synthesis of esters of polyene carboxylic acids starting from β,γ-unsaturated alcohols and malonic ester.

2) The structures of the compounds obtained have been confirmed by synthetic and physico-chemical methods.

LITERATURE CITED

[1] M. F. Carroll, J. Chem. Soc. 1940, 704, 1266; 1941, 507.

[2] W. Kimel, A. C. Cope, J. Am. Chem. Soc. 65, 1992 (1943).

[3] U. S. Patent 2395012 (1946); Ch. A. 40, 3130 (1946); U. S. Patent 2628250 (1953); Ch. A. 48, 710 (1954); 2638484 (1953); Ch. A. 48, 2763 (1954); U. S. Patent 2658911 (1953); Ch. A. 49, 1100 (1955); H. Normant, Ind. parf. 11, 172 (1956).

[4] C. Tavel, Helv. Chim. Acta 33, 1266 (1950).

[5] R. N. Lacey, J. Chem. Soc. 1954, 816; G. I. Samokhvalov, M. A. Miropolskaya and N. A. Preobrazhensky , Proc. Acad. Sci. USSR, 107,* 103 (1956).

[6] V. R. Naves, Comptes rend. 240, 1437 (1955); V. R. Naves, P. Ardizio, Bull. Soc. Chim. 1955, 1479; 1956, 678.

[7] V. R. Naves, P. Bachmann, Helv. Chim. Acta 30, 1599 (1947).

[8] I. K. Saricheva, G. A. Vorobyeva, A. S. Vasilenko, G. G. Vinokurova, S. A. Elkina and N. A. Preobrazhensky, J. Gen. Chem. 25, 1775 (1955).**

Received October 8, 1956

Institute of Fine Chemical Technology

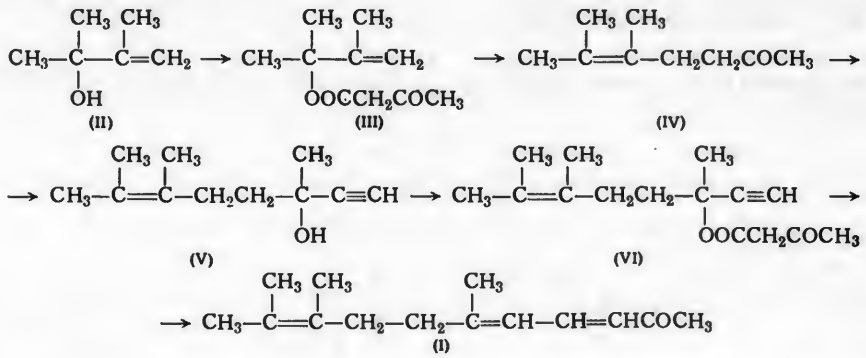
*See C. B. Translation.

**Original Russian pagination. See C. B. Translation.

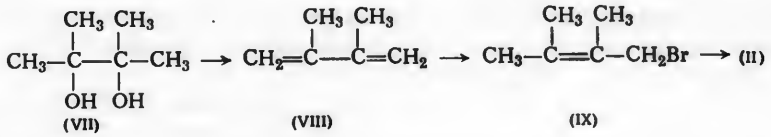
SYNTHESIS OF 2,3,6-TRIMETHYL-2,6,8-UNDECATRIEN-10-ONE (PSEUDOIRONE). 1L

I. K. Saricheva, G. A. Vorobyeva and N. A. Preobrazhensky

We have obtained pseudoirone (I) by a method using the ester of acetoacetic acid [1].



The starting material was 2,3-dimethyl-3-buten-2-ol, which was prepared by the method described in the literature from 1-bromo-2,3-dimethyl-2-butene (IX) [2], which in turn was obtained from pinacone (VII) via 2,3-dimethyl-1,3-butadiene (VIII) [3].



In order to get 2,3-dimethyl-2-hepten-6-one (IV), the 2,3-dimethyl-3-buten-2-ol (II) was made to react with diketene, and the acetoacetate (III) obtained was heated at 150-155°. As was expected, III underwent simultaneous decarboxylation and molecular rearrangement in the way desired. The 2,3-dimethyl-2-hepten-6-one (IV) produced in this way was further converted to 2,3,6-trimethyl-2-octen-7-yn-6-ol (V), which reacted with diketene to give the corresponding acetoacetate (VI). Compounds III-VI were characterized by their physicochemical constants and their infrared absorption spectra* (Fig. 1-4). The acetoacetate VI, like III, could be distilled in vacuo without decomposition, but, on heating it above 150° at normal pressure, carbon dioxide was evolved and molecular rearrangement occurred to give pseudoirone (I). To find out the time required for the completion of this rearrangement, the reactant was heated to 160-165°, and samples were taken at definite intervals for measurement of refractive index (see Table).

* The infrared spectra were obtained with an IKS-2 spectrometer (double beam model). The source of radiation was a globar. A sodium chloride prism was used over the range 700 -2000 cm^{-1} and lithium fluoride over the range 2200-4000 cm^{-1}. The slit width was controlled automatically.

Time (in minutes)	–	30	60	120	180	240	360	450	510
n_D^{20}	1.4742	1.4755	1.4825	1.4934	1.5050	1.5090	1.5115	1.5134	1.5134

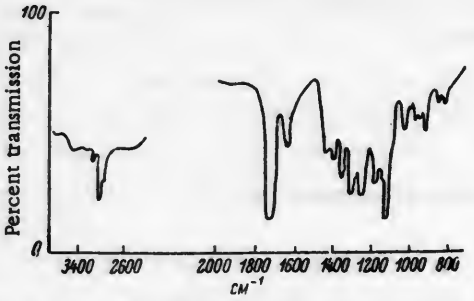


Fig. 1. Infrared spectrum of the acetate of 2,3-dimethyl-3-buten-2-ol.

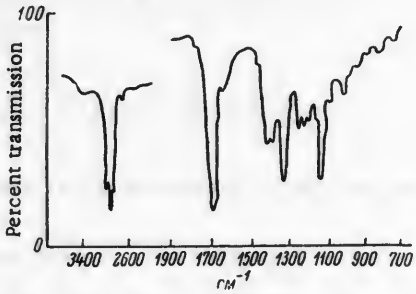


Fig. 2. Infrared spectrum of 2,3-dimethyl-2-hepten-6-one.

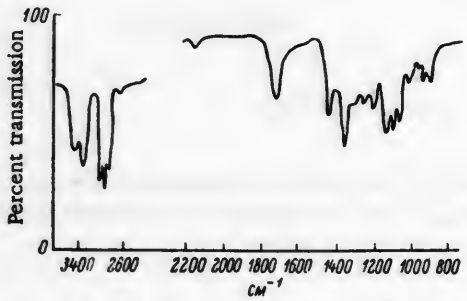


Fig. 3. Infrared spectrum of 2,3,6-trimethyl-2-octen-7-yn-6-ol.

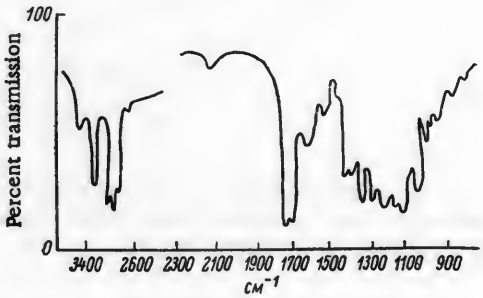


Fig. 4. Infrared spectrum of the acetoacetate 2,3,6-trimethyl-2-octen-7-yn-6-ol.

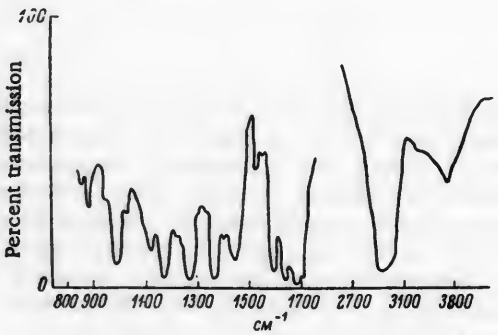


Fig. 5. Infrared spectrum of 2,3,6-trimethyl-2,6,8-undecatrien-10-one (pseudoirone).

The pseudoirone (I), obtained in 56% yield was characterized by its physical constants and its infrared absorption spectrum* (Fig. 5). The main absorption bands agreed with those quoted in the literature [4].

EXPERIMENTAL

1) 2,3-Dimethyl-3-buten-2-ol (II). 1-Bromo-2,3-dimethyl-2-butene (IX) (100 g, 0.613 mole) was

* The spectra were recorded by L. V. Lukyavov with a Hilger D-209 spectrophotometer (single beam model). The source of radiation was a Nernst filament. The cell was made from sodium chloride plates. The cell thickness was 30 μ.

stirred at room temperature for 18 hours with 1 liter of 10% aqueous sodium carbonate. The upper oily layer was then separated, and the lower layer was extracted with 300 ml of ether. The extract was combined with the upper layer and dried over calcium oxide. The ether was distilled off and the residue was redistilled in vacuo. Yield 41.3 g (67.2%).

B. p. 60-60.5° at 66 mm, n_D^{20} 1.4330, d_4^{20} 0.8545, MR_D 30.47, calc. for $C_6H_{12}O$ 30.96.

2) Acetoacetate of 2,3-dimethyl-3-buten-2-ol (III). Sodium (0.07 g, 0.003 g-atoms) was added to 20.2 g (0.202 mole) of II at room temperature. After 30 minutes the reaction mixture was cooled to 0°, a current of dry nitrogen was passed through, 21.8 g (0.260 mole) of freshly distilled diketene (b. p. 60.2-61° at 70 mm) was added over a period of 15 minutes, and the mixture was allowed to stand at 0° for 24 hours; 20 ml of saturated aqueous sodium bicarbonate was then added. The product was extracted with 300 ml of ether. The extract was dried over sodium sulfate. The solvent was distilled off, and the residue was redistilled in vacuo. Yield 25.75 g (70.9%).

B. p. 100.1-102° at 10 mm, n_D^{20} 1.4530, d_4^{20} 1.0120, MR_D 49.20, calc. for $C_{10}H_{16}O_3$ 49.57.

Found %: C 65.42, 60.48, H 8.50, 8.56. $C_{10}H_{16}O_3$. Calc. %: C 65.19, H 8.76.

Infrared spectrum – 3080 (weak), 2979 (v. strong), 2926 (weak), 1720 (v. strong), 1635 (strong), 1425 (medium), 1380 (strong), 1350 (v. strong), 1290 (strong), 1235 (strong), 1180 (medium), 1165 (medium), 1105 (v. strong), 1020 (strong), 970 (medium), 960 (medium), 900 (strong), 860 (medium), 810 (medium) cm^{-1}.

3) 2,3-Dimethyl-2-hepten-6-one (IV). The acetoacetate III (10 g) was heated in a current of dry nitrogen at an oil bath temperature of 150-155° for 7 hours, cooled to room temperature, dissolved in 50 ml of ether and treated with 10 ml of saturated aqueous sodium bicarbonate over a period of 30 minutes. The ether layer was dried over sodium sulfate. The ether was removed and the residue was redistilled in vacuo. Yield 4.5 g (59.2%).

B. p. 76-77° at 11 mm, n_D^{20} 1.4496, d_4^{20} 0.8690, MR_D 43.32, calc. for $C_9H_{16}O$ 43.31.

Infrared spectrum – 2978 (strong), 2926 (v. strong), 2856 (strong), 1700 (v. strong), 1640 (weak), 1435 (medium), 1385 (medium), 1350 (v. strong), 1250 (medium), 1210 (weak), 1135 (v. strong), 1115 (weak), 940 (weak), 895 (weak), 835 (weak), 740 (weak) cm^{-1}.

2,4-Dinitrophenylhydrazone. B. p. 97-98.5° (from alcohol).

Found %: C 56.49, H 5.87, N 17.57. $C_{15}H_{20}O_4N_4$. Calc. %: C 56.20, H 6.30, N 17.50.

4) 2,3,6-Trimethyl-1-octen-7-yn-6-ol (V). A vigorous stream of dry acetylene was passed through 400 ml of anhydrous liquid ammonia, the liquid was well stirred, and 8.1 g (0.44 g-atoms) of sodium was added at such a rate that no persistent blue coloration occurred. Then 47 g (0.34 mole) of IV was added, drop by drop, over a period of 30 minutes, and the whole was allowed to stand for 12 hours at room temperature. The viscous dark-orange product was cooled to 0°, treated with 150 ml of iced water and then with 55 ml of 50% sulfuric acid, and extracted with 500 ml of ether. The extract was dried over sodium sulfate. The ether was distilled off, and the residue was redistilled in vacuo. Yield 42.8 g (76.8%).

B. p. 90.3-93° at 9 mm, n_D^{20} 1.4692, d_4^{20} 0.8966, MR_D 51.68, calc. for $C_{11}H_{18}O$ 51.98.

Found %: C 79.97, 79.38, H 10.71, 10.64. $C_{11}H_{18}O$. Calc. % C 79.47, H 10.91.

Infrared spectrum – 3410 (strong), 3300 (v. strong), 2979 (strong), 2926 (v. strong), 2856 (strong), 2145 (weak), 1710 (strong), 1435 (strong), 1350 (v. strong), 1260 (medium), 1206 (strong), 1140 (strong), 1098 (strong), 1060 (strong), 1030 (medium), 980 (strong), 965 (weak), 905 (weak) cm^{-1}.

5) The acetoacetate of 2,3,6-trimethyl-2-octen-7-yn-6-ol (VI). The reaction mixture, obtained by the interaction of 0.04 g (0.002 g-atoms) of sodium with 20 g (0.120 mole) of V, was cooled to 0°, stirred vigorously in a current of dry nitrogen, and treated, drop by drop, with 13 g (0.155 mole) of freshly distilled diketene over a period of 20 minutes. After further stirring for 5 hours at 0° and standing for 20 hours at the same temperature, the reaction mixture was treated with 15 ml of saturated aqueous sodium bicarbonate. The product was extracted with 300 ml of ether. The ethereal extract was dried over sodium sulfate. The solvent was distilled off, and the residue was redistilled in vacuo. Yield 25 g (86.4%).

B. p. 119.5-120° at 1.2 mm, n_D^{20} 1.4742, d_4^{20} 0.9977, MR_D 70.53. Calc. for $C_{15}H_{22}O_3$ 70.60.

Found %: C 72.16, 71.96, H 8.71, 8.61. $C_{15}H_{22}O_3$. Calc. %: C 71.96, H 8.85.

Infrared spectrum – 3330 (strong), 3260 (v. strong), 2975 (v. strong), 2920 (v. strong), 2856 (v. strong), 2120 (weak), 1720 (v. strong), 1700 (v. strong), 1610 (strong), 1530 (weak), 1435 (medium), 1385 (medium), 1350 (v. strong), 1290 (v. strong), 1220 (v. strong), 1150 (strong), 1130 (strong), 1055 (medium), 1010 (medium), 960 (weak), 860 (weak), 740 (weak), 695 (weak), cm^{-1}.

6) 2,3,6-Trimethyl-2,6,8-undecatrien-10-one (pseudoirone) (I). The acetoacetate of VI (10 g, 0.04 mole, n_D^{20} 1.4742) was heated in a current of nitrogen at a bath temperature of 160-165° for 7.5 hours. The end of the reaction was determined by the change in refractive index (n_D^{20} 1.5134) and the considerable reduction in the rate of evolution of carbon dioxide (test with baryta water). The reaction mixture was cooled to room temperature, dissolved in 50 ml of ether and carefully stirred for 30 minutes with 10 ml of saturated aqueous sodium bicarbonate. The solvent was distilled off, and the residue was redistilled in vacuo. Yield 4.65 g (56.4%).

B. p. 100.1-102° at 0.4 mm, n_D^{20} 1.5228, d_4^{20} 0.9208, MR_D 68.41, calc. for $C_{14}H_{22}O$ 65.46.

Found %: C 81.11, 81.55, H 10.46, 10.50, $C_{14}H_{22}O$. Calc. %: C 81.49, H 10.75.

Infrared spectrum – 3450 (strong), 2926 (strong), 1700 (v. strong), 1680 (v. strong), 1650 (v. strong), 1600 (v. strong), 1530 (medium), 1450 (strong), 1380 (v. strong), 1270 (strong), 1240 (strong), 1170 (v. strong), 1120 (medium), 1000 (strong), 960 (medium), 890 (medium) 860 (medium) cm^{-1}.

Semicarbazone. M. p. 165-166.2° (from alcohol).

2,4-Dinitrophenylhydrazone. M. p. 148-150° (from a mixture of alcohol and ethyl acetate).

Found %: C 62.44, 61.79, H 6.80, 6.48, N 14.43. $C_{20}H_{26}O_4N_4$. Calc. %: C 62.16, H 6.78, N 14.50.

SUMMARY

1) A new synthesis of 2,3,6-trimethyl-2,6,8-undecatrien-10-one (pseudoirone) has been developed, starting from 2,3-dimethyl-1,3-butadiene and involving a number of stages.

2) In the course of the synthesis the acetoacetates of 2,3-dimethyl-3-buten-2-ol and 2,3,6-trimethyl-2-octen-7-yn-6-ol were prepared and characterized, and a new method was developed for making 1,3-dimethyl-2-hepten-6-one.

LITERATURE CITED

[1] G. I. Samokhvalov, M. A. Miropolskaya and N. A. Preobrazhensky, Proc. Acad. Sci. USSR, 107, 103 (1956).•

[2] L. Claisen, J. pr. Ch. 105, 65 (1922).

[3] B. A. Kilby, F. B. Kipping, J. Chem. Soc. 1939, 437; L. Ruzicka, C. F. Seidel, H. Schinz, C. Tavel, Helv. Chim. Acta 30, 1810 (1947).

[4] V. R. Naves, Bull. Soc. Chim. 1950, 793; 1954, 667; N. A. Slovokhotova, G. I. Samokhvalov, G. M. Kunitskaya and M. A. Miropolskaya, J. Gen. Chem. 24, 2222 (1954).•

Received October 8, 1956

Institute of Fine Chemical Technology

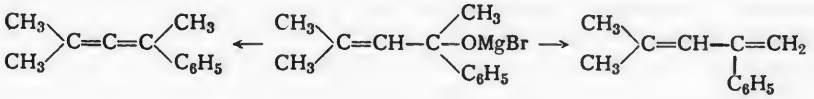
• Original Russian pagination. See C. B. Translation.

THE CHEMICAL STRUCTURE OF THE HYDROCARBON $C_{12}H_{14}$ AND THE SYNTHESIS OF NEW PHENYLATED 1,3-DIENE HYDROCARBONS. VII.

V. I. Esafov

From mesityl oxide and phenyl magnesium bromide, Klages [1] obtained a 44.6% yield of a hydrocarbon of composition $C_{12}H_{14}$ with a b. p. of 107-108° at 20 mm, $d_4^{19.8}$ 0.9277, n_D^{20} 1.5236, and assumed it to be trimethylphenylallene, because, on oxidation with permanganate and sulfuric acid, it gave a 39.5% yield of acetophenone. Later, Ingold and Wilson [2] repeated the reaction and obtained instead of methylisocrotylphenylcarbinol the hydrocarbon $C_{12}H_{14}$, but they assumed this to be α,α-dimethyl-γ-phenylbutadiene, since, on ozonolysis, it gave formaldehyde, benzoic acid and a neutral substance which showed the iodoform reaction. Ravier [3] succeeded in obtaining methylisocrotylphenylcarbinol and from it, by dehydration, the hydrocarbon $C_{12}H_{14}$, which he believed to be a diene with a conjugated system of double bonds. A small quantity of a hydrocarbon $C_{12}H_{14}$ was obtained even when the reaction between mesityl oxide and phenyl magnesium bromide was carried out under severe conditions [4]. A. I. Zakharova [5] investigated the reaction between 2-methyl-2-chloro-3-pentene and phenyl magnesium bromide and obtained a hydrocarbon $C_{12}H_{14}$ of b. p. 106-108° at 20 mm, d_4^{20} 0.9302, and n_D^{20} 1.5470. This was shown to be the expected 2-methyl-2-phenyl-3-heptene but a diene hydrocarbon which would not react with maleic anhydride. Oxidation of this hydrocarbon with 1% aqueous permanganate gave acetone, acetophenone and some acetic and benzoic acids. Since this hydrocarbon closely resembled Klages' hydrocarbon in its physical constants and properties, Zakharova presumed it to be trimethylphenylallene. Zakharova also showed that the hydrocarbon $C_{12}H_{14}$ had a fairly high boiling point, so that it could not be present in fractions boiling between 78 and 145°, as we have reported [4]. Her criticism loses force, however, as we did not give any values for the physical constants of the hydrocarbon $C_{12}H_{14}$. We merely noted its presence in the fraction boiling between 78 and 145°, where it was carried over by the vapors of lower boiling hydrocarbons on distillation from sodium in a current of CO_2. Thus there were two views as to the structure of the hydrocarbon, not excluding the third possibility that it was a mixture of allene and 1,3-diene hydrocarbons. It was desirable to find out which of these theories was correct.

The reaction between mesityl oxide and phenyl magnesium bromide is carried out at −15° and, in spite of this, the main product is a hydrocarbon and not a carbinol. Thus, in the course of the reaction the intermediate Grignard bromomagnesium carbinolate splits off HOMgBr, and this can happen in two ways, the first of which is in agreement with the Zaitsev−Wagner rule.

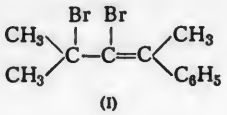


This makes it clear why about 24% of the ketone* does not take part in the reaction when equimolecular quantities of mesityl oxide and phenyl magnesium bromide are used, because part of the phenyl magnesium bromide is decomposed by the HOMgBr which splits off. Since a hydrocarbon, or a mixture of carbinol and hydrocarbon, is very often obtained instead of a carbinol by the reaction of α,β unsaturated ketones with RMgX [6], the phenomenon discussed must be recognized as having a general character with this type of ketone. Thus, in order to avoid unsatisfactory results when determining the extent of enolysis of an α,β unsaturated ketone, it is necessary to take into account the above mentioned phenomenon, which has previously been completely ignored.

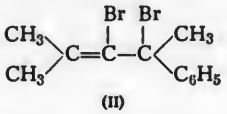
* Part of the mesityl oxide may also be in the enol form.

The value of the molecular refraction, showing considerable exaltation, cannot be used as a criterion for deciding the structure of the hydrocarbon $C_{12}H_{14}$, as the allene structure can also be represented as a disubstituted styrene [7]. Experiment showed that the value of the molecular refraction was somewhat reduced at the elevated temperature at which it was determined.

In order to elucidate the structure of $C_{12}H_{14}$, the properties of the dibromide were investigated first. The allene structure would be expected to give two isomeric dibromides – I and II.

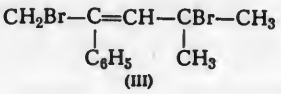


(I)

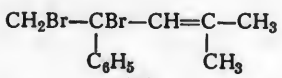


(II)

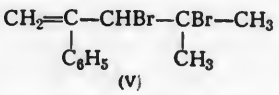
The 1,3-diene structure could give three isomeric dibromides – III, IV and V.



(III)



(IV)



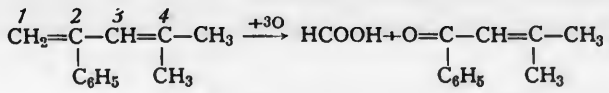
(V)

The dibromides I, II and V should give off HBr in the process of their formation (Lvova–Tishchenko reaction), IV should do this to a lesser extent, while III should be the most stable. When $C_{12}H_{14}$ was brominated with 50% of normal bromine (Table 1, Experiment 1), the production of HBr was 3.5% of the total consumption of bromine, indicating that the dibromide was relatively stable. Further evidence was obtained by oxidizing a specially prepared sample of the dibromide with permanganate. The dibromide I should give acetophenone, in an amount not less than that obtained by oxidizing the original hydrocarbon, and α-bromoisobutyric acid or metacrylic* acid. The dibromide II should give acetone, to the same extent as in the oxidation of $C_{12}H_{14}$, and α-phenyl-α-bromopropionic acid or atropic* acid. In fact the main product was a neutral substance with strongly lachrymatory and irritant properties, together with some acetone and benzoic and formic acids. This all indicated that the structure of $C_{12}H_{14}Br_2$ corresponded to 2-phenyl-4-methyl-1,3-pentadiene and not to trimethylphenylallene. But the most convincing demonstration of the structure of $C_{12}H_{14}$ was given by the Diels–Alder reaction. The hydrocarbon dissolved maleic anhydride, producing a greenish-yellow coloration, and reacted with it exothermically. 6,6-Dimethyl-4-phenyl-4-cyclohexene-1,2-dicarboxylic acid was found in the reaction products.

When the hydrocarbon $C_{12}H_{14}$ was oxidized with permanganate the following were detected in the products – acetone, acetophenone, carbonic acid, and benzoic acids and also formic acid. The latter could only have come from a $CH_2=C<$ grouping, which would only be found in the 1,3-diene.

The only formally contradictory fact is the formation of acetophenone by the oxidation of $C_{12}H_{14}$. We are inclined to explain this as the result of an anomalous course of the oxidation reaction, accompanied by hydration of the ethylenic linkage. Butlerov first observed dehydration and hydration of the ethylenic linkage in the oxidation of tertiary alcohols by chromic acid. Isobutyric acid [8] was obtained, together with other products, by the oxidation of trimethylcarbinol, and octylic acid [9] by the oxidation of diisobutylene. Similar examples are known for oxidations occurring in the presence of potassium permanganate. For instance, uric acid is oxidized to allantoin. T. A. Favorskaya and N. V. Shcherbinskaya [10] have recently observed the hydration of a double bond between secondary and tertiary carbon atoms during oxidation by potassium permanganate. The formation of acetophenone from 2-phenyl-4-methyl-1,3-pentadiene can be explained as follows – if oxidative degradation occurs first at the 1,2 double bond, the products will be formic (carbonic) acid and the α,β-unsaturated ketone isopropylidenacetophenone.

* Under the conditions for the Lvova–Tishchenko reaction.



Under the alkaline conditions which prevail in $KMnO_4$ oxidation, the latter is hydrated and converted into the β-ketol $C_6H_5COCH_2C(OH)(CH_3)_2$, which is capable of hydrolytic decomposition to acetophenone and acetone. It is impossible to exclude the possibility of such a process, in which the 3,4 double bond joining secondary and tertiary carbon atoms in $C_{12}H_{14}$ is hydrated, either before or simultaneously with oxidative degradation, leading eventually to the formation of the above mentioned β-ketol. Finally, in order to settle the question, 2-phenyl-3-methyl-3-hepten-2-ol was specially synthesized, and from this was prepared 2-phenyl-3-methyl-1,3-pentadiene which cannot have an allene structure. The isomeric $C_{12}H_{14}$ hydrocarbons were investigated spectroscopically by P. P. Shorigin and V. M. Medvedeva.* The Raman spectra of the two hydrocarbons were similar; the allene group was not detectable in the hydrocarbon prepared from mesityl oxide. This showed quite definitely that the latter hydrocarbon was 2-phenyl-4-methyl-1,3-pentadiene, and that it only contained a small amount, if any, of trimethylphenylallene.

The effects of substituents, including phenyl, on the ease of attack of the double bonds was investigated by brominating the isomeric hydrocarbons $C_{12}H_{14}$ and a synthetic sample of 2-phenyl-3,4-dimethyl-1,3-hexadiene (Table 1). Using 50% of the bromine equivalent, there was only a small evolution of HBr (3.5-4%) from 2-phenyl-4-methyl-1,3-pentadiene (Experiment 1) and from 2-phenyl-3-methyl-1,3-pentadiene (Experiment 3), and the results could only be explained by supposing that bromine added preferentially at the 1 and 4 positions, and to an even greater extent with the second hydrocarbon. When the amount of bromine was increased to 100% of that required to saturate the double bonds, the two isomeric $C_{12}H_{14}$ hydrocarbons behaved differently. The dibromide of 2-phenyl-4-methyl-1,3-pentadiene took up a considerable quantity of bromine, giving the unstable tetrabromide, and evolved 15% of the bromine in the form of HBr (Experiment 2), while the dibromide of 2-phenyl-3-methyl-1,3-pentadiene took up very little bromine, and the evolution of HBr was increased by 2% (Experiment 4).

In 2-phenyl-3-methyl-1,3-pentadiene the substituent groups are arranged more symmetrically, with respect to the conjugate system, and there is a greater degree of conjugation of the ethylenic linkages than in 2-phenyl-4-methyl-1,3-pentadiene. These data on the bromination of phenylated 1,3-dienes served to confirm the previously enunciated empirical rules [11]. As was expected, the least degree of conjugation of the ethylenic bonds was shown by 2-phenyl-3,4-dimethyl-1,3-hexadiene, since in this molecule three of the carbon atoms composing the conjugated system carry substituent groups, and this is known to increase the independence of the ethylenic linkages. On 50% bromination of the double bonds of this hydrocarbon, the bromine added preferentially to the 3,4 bond, which may explain the considerable evolution (up to 22%) of bromine in the form of HBr (Experiment 5).

EXPERIMENTAL

1. Investigation of the reaction between mesityl oxide and phenyl magnesium bromide (with the assistance of the students O. G. Boyarshinova, M. I. Ermakova, G. F. Siromyatnikova, M. A. Plashkina and Yu. N. Ellanska). The reaction was carried out in a previously described [11] apparatus at −15°. A 1:1 solution of 66 g of mesityl oxide in dry ether and a solution of phenyl magnesium bromide, prepared from 16 g of magnesium and 110 g of bromobenzene in 150 ml of dry ether, were added to 150 ml of dry ether over a period of 6 hours. The reaction mixture was then stirred without cooling for 1 hour and carefully decomposed with 100 ml of iced water and ammonium chloride solution. The product was extracted in the usual way and distilled at 20 mm. This gave a recovery of 16 g of mesityl oxide (average of 8 experiments). Crystals of iodine were added to the residue, and distillation was continued at 20 mm to dehydrate the 2-methyl-4-phenyl-2-penten-4-ol, but very little water was evolved. The hydrocarbon was purified by distillation over metallic sodium at 6 mm. The total products were:

First fraction, b. p. 87-88°, 38 g, d_4^{20} 0.9242, n_D^{20} 1.5425, MR_D 53.92; 2nd fraction, b. p. 88-92°, 3.0 g, d_4^{20} 0.9308, n_D^{20} 1.5470. MR_D calc. for $C_{12}H_{14}$ 53.08.

The result of the synthesis was the hydrocarbon $C_{12}H_{14}$ in 47% yield (1st fraction) instead of the carbinol

* We take this opportunity of thanking them.

2-methyl-4-phenyl-2-hepten-4-ol. By carrying out the reaction under the same conditions, but with one and a half times the quantity of phenyl magnesium bromide, the yield of $C_{12}H_{14}$ was increased to 60%. The hydrocarbon had the following properties:

d_4^{30} 0.9129, n_D^{20} 1.5389, MR_D 54.24, d_4^{70} 0.8811, n_D^{70} 1.5153, MR_D 54.11.

2. Investigation of the structure of the hydrocarbon $C_{12}H_{14}$.

a) The bromination of the hydrocarbon was carried out under the conditions previously described [12]. For the sake of brevity the results are shown together in Table 1.

TABLE 1

No. of experiments	Weight taken in g	Volume of Br in CCl_4 solution in ml	Volume of 0.1 N $Na_2S_2O_3$ solution in ml			Iodine number (theoretical)	Observed value of iodine number			Conversion of bromine into HBr as % of total consumption of bromine
			Titration of excess halogen	Corresponding consumption of halogen	Titration of iodine from HI		Total	Eliminated	Additional	
2-Phenyl-4-methyl-1,3-pentadiene										
1	0.0848	2.5	0.04	10.67	0.37	320.86	159.71	11.07	148.64	3.46
2	0.0786	5.0	6.82	14.60	2.22		235.77	71.70	164.07	15.20
2-Phenyl-3-methyl-1,3-pentadiene										
3	0.0864	2.92	1.18	10.29	0.44	320.86	151.17	12.92	138.25	4.27
4	0.0784	5.10	10.14	9.89	0.64		160.12	20.72	139.40	6.47
2-Phenyl-3,4-dimethyl-1,3-hexadiene										
5	0.1171	3.3	0.16	11.95	2.60	272.55	129.53	56.36	73.17	21.75
6	0.1148	6.6	6.72	17.50	4.56		193.48	100.83	92.65	26.05

b) The iodine number was determined by the method of Margoshes, using a 337% excess of 0.5 N alcoholic iodine; it was found to be equal to 304.6.

c) Oxidation of $C_{12}H_{14}Br_2$ with potassium permanganate. A solution of 5.5 g of dry bromine in 20 ml of CCl_4 was added, drop by drop, with constant stirring, over a period of 3.5 hours, to a solution of 5 g of $C_{12}H_{14}$ in 20 ml of dry CCl_4 at −15 to −17°. The CCl_4 was then distilled off in vacuo at 25°. The dibromide, a transparent pale-yellow oil, was analyzed.

Found %: Br 49.79. Calc. for $C_{12}H_{14}Br_2$ %: Br 50.25.

$C_{12}H_{14}Br_2$ (10 g) was mixed with 100 g of finely crushed ice, and 10 g of finely powdered permanganate was added in 10 portions together with 150 ml of iced water. The reaction mixture was vigorously shaken while this was going on, and the whole was then allowed to stand on ice for 20 hours. To complete the decomposition of the permanganate it was necessary to add 3.6 g of $Na_2SO_3 \cdot 5H_2O$, so that 1.75 g of permanganate did not take part in the reaction. The residue of manganese dioxide was filtered off and washed several times with hot water. The filtrate was distilled. A sample from the total distillate of 495 ml was analyzed by the iodoform reaction and gave the following results – in a blank experiment 25 ml of iodine solution required 23.28 ml of 0.1 N $Na_2S_2O_3$. A mixture of 10 ml of the distillate and 25 ml of the iodine solution required 22.78 ml of 0.1 N $Na_2S_2O_3$. This corresponded to 0.2394 g of acetone.

The residue from the distillation of the neutral material, which had an alkaline reaction, was decomposed with dilute (1 : 8) sulfuric acid, and the organic acids were steam distilled. Benzoic acid (0.3 g) of m. p. 121° was found in the acid distillate. The filtrate from this showed a positive reaction for formic acid. Since the recovery of oxidation products was poor, the residue of manganese dioxide, which had been washed three times, was

extracted for 24 hours with ether. The product, after filtration, drying and distilling off the ether, was 4.5 g of a heavy oil with an acrid smell and strongly lachrymatory properties. The oil gave a positive Beilstein reaction and a precipitate with an alcoholic solution of $AgNO_3$.

d) Investigation of the reaction of $C_{12}H_{14}$ with maleic anhydride. Freshly distilled maleic anhydride (2 g) was added to 3 g of the hydrocarbon, and there appeared the yellowish-green coloration characteristic of diene hydrocarbons with conjugated systems of double bonds. When the mixture was heated to 75° an exothermic reaction occurred, leading to boiling and a rise in temperature to 175°. The product was cooled and boiled with a dilute solution of KOH, and the solution of potassium salts was filtered to remove a small amount of oil, and decomposed with dilute sulfuric acid. The heavy oily product was boiled with water until the residue on cooling turned into a brittle solid. This was recrystallized twice from dilute alcohol to give 1.4 g of a substance of m. p. 185° (decomp). The latter was recrystallized from alcohol to give a final product of m. p. 197° (decomp).

Found acid number 403.14, mol. wt. 275.8 (Rast). Calc. for $C_{16}H_{18}O_4$ acid number 409.09, mol. wt. 274.3.

On the basis of this analysis the substance of m. p. 197° was considered to be 6,6-dimethyl-4-phenyl-4-cyclohexen-1,2-dicarboxylic acid.

e) Oxidation of $C_{12}H_{14}$ with potassium permanganate. The hydrocarbon (5 g) was oxidized under the same conditions (section b above) as were used for the dibromide. 14 g of $KMnO_4$ and 200 ml of iced water were used. At the end of the reaction the permanganate was all decomposed; the residual manganese dioxide was filtered off and washed with cold and then with boiling water. The filtrate was distilled to remove the neutral oxidation products from the potassium salts. The distillate (490 ml) contained drops of heavy oil. To isolate the oil, the distillate was saturated with NaCl and further distilled, selecting the first third of the volume of distillate. After three such operations, 3.0 g of an oil with a smell of acetophenone was obtained, and this gave 1.48 g of a semicarbazone of m. p. 198°. After the removal of the acetophenone, the aqueous solution was distilled again, and the first third of the distillate was selected. Addition of potash to this caused the separation of a colorless liquid layer with a small of acetone, from which a bisulfite compound was obtained. The residue from the distillation of the neutral compounds had an alkaline reaction, and was decomposed with dilute sulfuric acid. CO_2 was evolved. Organic acids were then steam distilled over. A solid acid was filtered off from the distillate after standing for 6 hours in the cold. After recrystallization from alcohol, this had an m. p. of 121° and gave no depression when mixed with chemically pure benzoic acid. The filtrate showed a positive reaction for formic acid. Neutralization of 1 ml of filtrate required 2.68 ml of 0.1 N KOH, which corresponded to a 0.62 g yield of formic acid. The formic acid in the filtrate was destroyed by heating with $KMnO_4$ solution. An aqueous acid solution was obtained containing mainly acetic acid.

Found % Ag 64.10. Calc. % for $C_2H_3O_2$ Ag 64.67

Thus the products of oxidation of $C_{12}H_{14}$ were acetone, acetophenone, and formic, acetic, benzoic and carbonic acids.

3. Investigation of the reaction between 3-methyl-2-hepten-4-one and phenyl magnesium bromide (with the assistance of the student V. Ya. Kleiman). The reaction was performed in the same way as for the above synthesis based on mesityl oxide, except that the 1:1 ethereal solution of 60 g of 3-methyl-2-hepten-4-one (m. p. 137.5-139.5° at 747 mm, d_4^{20} 0.8741, n_D^{20} 1.4525) was added, drop by drop, over a period of 1.5 hours, and the solution of phenyl magnesium bromide, prepared from 24 g of magnesium, 165 g of bromobenzene and 300 ml of dry ether, was added over 3.5 hours. The reaction mixture was left for 20 hours and worked up as previously described. The final products were two fractions. The 1st fraction, amounting to 18 g, had a b. p. of 84° at 5.5 mm (over sodium).

d_4^{20} 0.9302, n_D^{20} 1.5450, MR_D 53.78, calc. for $C_{12}H_{14}$ 53.08.

The iodine number of this hydrocarbon was measured by the bromination method (Table 1, Experiments 3 and 4). The hydrocarbon dissolved maleic anhydride to give a characteristic yellow-green color; on heating the mixture to 63°, there was an exothermic reaction, and the temperature rose to 167°. The yield of 2-phenyl-3-methyl-1,3-pentadiene was 18.6%.

The 2nd fraction (9 g) had a b. p. of 100-102° at 4 mm.

d_4^{20} 0.9913, n_D^{20} 1.5311, MR_D 55.01, calc. for $C_{12}H_{16}O$ 55.07.

TABLE 2

2-Phenyl-4-methyl-1,3-pentadiene		2-Phenyl-3-methyl-1,3-pentadiene		Designation
Frequency in cm^{-1}	Intensity	Frequency in cm^{-1}	Intensity	
3055	Weak, broad	3053	Weak, broad	C−H linkage
2971	Weak	–	–	
2916	Weak	2919	Weak	
1638.8	210 Units	1634.0	320 Units	> C=C < linkage
1600	260 Units	1603.1	330 Units	Benzene ring
–		1383	Weak	–
–	—	1310	Weak	–
1028	Weak	–	–	–
1002.0	Medium	1002.5	Medium	Benzene ring

The material decolorized a solution of bromine in CCl_4. When distilled at 30 mm in the presence of iodine, it lost water to form 2-phenyl-3-methyl-1,3-pentadiene. The physico-chemical constants and the properties of this substance showed it to be the normal product of Grignard reaction – 2-phenyl-3-methyl-3-hepten-2-ol. The yield of carbinol was 8.3%.

4) Investigation of the reaction between 3,4-dimethyl-3-hexen -5-one and phenyl magnesium bromide (with the assistance of the student T. A. Sharifullina). The reaction was carried out at −15°. A 1 :1 ethereal solution of 30 g of 3,4-dimethyl-3-hexen-5-one and a solution of phenyl magnesium bromide, obtained from 8.6 g of magnesium, 62 g of bromobenzene and 140 ml of dry ether, were added, drop by drop, with constant stirring, to 100 ml of dry ether over a period of 5 hours. The reaction mixture was allowed to stand overnight and then decomposed with ice water and ammonium chloride solution. Fractional distillation gave two fractions.

First fraction, b. p. 90° at 3 mm, 12 g, d_4^{20} 0.9195, n_D^{20} 1.5318, MR_D 62.75, calc. for $C_{14}H_{18}$ 62.31.

The yield of 2-phenyl-3,4-dimethyl-1,3-hexadiene was 27%. The data on the bromination of this hydrocarbon is given in Table 1, Experiments 5 and 6. The hydrocarbon dissolved maleic anhydride to give a weak yellowish-green coloration.

Second fraction, b. p. 103-105° at 2 mm, 8.5 g, d_4^{20} 0.9613, n_D^{20} 1.5240, MR_D 64.80, calc. for $C_{14}H_{20}O$ 64.31.

The yield of 2-phenyl-3,4-dimethyl-3-hexen-2-ol was 17.5%. When the carbinol was distilled with a crystal of iodine at 20 mm, it lost water and was converted into the above hydrocarbon.

5. Spectroscopic investigation of the isomeric hydrocarbon $C_{12}H_{14}$.* The Raman spectra were obtained with a three-prism spectrograph NSP-51, with a linear dispersion of 29 A/mm in the region of 4400 A. The slit width was 0.1 mm, corresponding to 10.09 cm^{-1}. The intensities of the Raman lines were determined by photometry of the photographs (the accuracy was about 10% of the value measured). The unit of intensity was taken as 0.01 of that of the strongest CCl_4 line at 313 cm^{-1} (calculated to equal molar concentrations). The frequencies were determined with the pure liquid hydrocarbons; the intensities were measured using solutions in CCl_4, the lines of the latter serving as internal standards.

The spectra showed that the hydrocarbon obtained from mesityl oxide and phenyl magnesium bromide, whose structural formula it was required to determine, gave the characteristic frequency of >C=C< in the region 1630 cm^{-1} and not that of the allene group in the region 1100 cm^{-1}, but this was not indisputable evidence for the absence of the allene form** since the spectra of allene compounds with complex systems of conjugated bonds have not been very well investigated.

Table 2 shows that the spectra of the isomeric $C_{12}H_{14}$ hydrocarbons were very similar. The weakest lines were not measured. Thus the spectral data supported the view that the structural formula of the above mentioned hydrocarbon was 2-phenyl-4-methyl-1,3-pentadiene.

* This section was written by P. P. Shorygin and V. M. Medvedeva.

** A small percentage of the allene form would not have been detected.

The intensity of the line in the region of 1630 cm^{-1} for 2-phenyl-3-methyl-1,3-pentadiene was lower than that of the >C=C< line for styrene (about 300 units). The intensity of this line for 2-phenyl-4-methyl-1,3-pentadiene was somewhat lower still. The structural features of 2-phenyl-4-methyl-1,3-pentadiene give grounds for believing that its molar intensity coefficient should be greater than that of 2-phenyl-3-methyl-1,3-pentadiene. Further investigation would be necessary to find out the reason for this reduction in intensity.

SUMMARY

1) It is found as a general rule for α,β-unsaturated ketones that, in the course of their reaction with a Grignard reagent, the halogenomagnesium carbinolate is capable of splitting off HOMgX, which decomposes RMgX. For this reason, and also because of the enolization of the ketone, it is necessary to use an excess of Grignard reagent to get the maximum yield of product.

2) It is shown that, when determining the percentage enolization of an α,β-unsaturated ketone, it is necessary to correct for the formation of HOMgX by the halogenomagnesium carbinolate.

3) It is shown, on the basis of physico-chemical properties and spectroscopic investigation, that the hydrocarbon $C_{12}H_{14}$, obtained by the reaction of mesityl oxide with phenyl magnesium bromide, is 2-phenyl-4-methyl-1,3-pentadiene and not trimethylphenylallene.

4) The new α,β-unsaturated tertiary alcohols – 2-phenyl-3-methyl-3-penten-2-ol and 2-phenyl-3,4-dimethyl-3-hexen-2-ol – have been prepared and their physico-chemical constants determined.

5) Two new phenylated 1,3-diene hydrocarbons – 2-phenyl-3-methyl-1,3-pentadiene and 2-phenyl-3,4-dimethyl-1,3-hexadiene – have been prepared, their physico-chemical constants recorded and their behavior on bromination investigated.

LITERATURE CITED

[1] A. Klages, Ber. 37, 2301 (1904).

[2] C. K. Ingold and C. L. Wilson, J. Chem. Soc. 1933, 1493.

[3] H. Ravier, Comptes. rend. 198, 1786 (1934).

[4] V. I. Esafov, J. Gen. Chem. 9, 467 (1939).

[5] A. I. Zakharova, J. Gen. Chem. 17, 1277 (1947).

[6] V. I. Esavov and M. V. Smirnov, J. Gen. Chem. 10, 1535 (1940); V. I. Esafov et al., J. Gen. Chem. 13, 818 (1943); V. I. Esafov, J. Gen. Chem. 19, 1063 (1949).•

[7] K. Auwers and F. Eisenlohr, J. pr. Ch. 82, 91 (1910).

[8] A. M. Butlerov, J. Russ. Chem. Soc. 3, 277 (1871).

[9] A. M. Butlerov, J. Russ. Chem. Soc. 9, 38 (1877).

[10] T. A. Favorskaya and M. V. Shcherbinskaya, J. Gen. Chem. 23, 1667 (1953).•

[11] V. I. Esafov, J. Gen. Chem. 19, 1065 (1949).

[12] V. I. Esafov, J. Gen. Chem. 17, 1453 (1947).

Received October 1, 1956

Ural State University

• Original Russian pagination. See C. B. Translation.

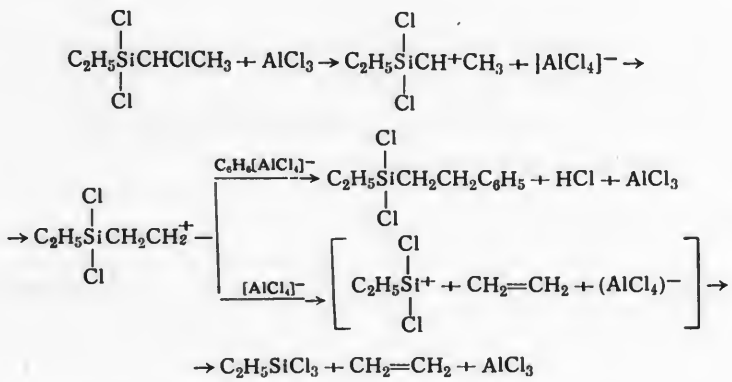
THE REACTION OF CHLOROALKYLALKYLDICHLOROSILANES WITH AROMATIC COMPOUNDS IN THE PRESENCE OF $AlCl_3$

E. A. Chernyshev, M. E. Dolgaya and Yu. P. Egorov

In a previous paper we reported the development of a method of silicoalkylation of aromatic compounds with α- and β-chloroalkyltrichlorosilanes [1]. It seemed interesting to use chloroalkylalkyldichlorosilanes as silicoalkylating agents as this would make it possible to synthesize various silane chlorides with two hydrolyzable groups at the silicon. It seemed probable that these reactions would be difficult to carry out as under the effect of $AlCl_3$, α-chloroalkylalkyldichlorosilanes are readily rearranged into alkyltrichlorosilanes [2], while β-chloroalkylalkyldichlorosilanes undergo β-decomposition [3]. However, a preliminary experiment reacting β-chloroethylethyldichlorosilane with benzene showed that there was practically no β-decomposition of this chloride in a benzene medium and that silicoalkylation took place. Furthermore, it was found that the rate of the reaction in this case was considerably greater than the rate of the reaction of benzene with β-chloroethyltrichlorosilane. The reaction proceeded very vigorously with the evolution of heat and was complete after several hours. Silicoalkylation of chlorobenzene and toluene proceeded as vigorously. The yields in these reactions were about 40% and in separate cases increased to 60-70%.

Without solvent and in the presence of $AlCl_3$, both β- and α-chloroethylethyldichlorosilanes were decomposed quantitatively in a few minutes with the formation of ethyltrichlorosilane and the evolution of ethylene. However, α-chloroethylethyldichlorosilane also silicoalkylated benzene, toluene and chlorobenzene and no evolution of ethylene was observed in the reaction, i.e., there was not even partial decomposition.

In silicoalkylation of aromatic compounds with α-chloroethylethyldichlorosilane, as spectral investigations showed, the only substances formed were those with an aromatic ring in a position β to the silicon atom. Apparently, the reaction of α-chloroethylethyldichlorosilane with $AlCl_3$ with or without aromatic compounds being present proceeds by the following scheme:



It was interesting that, in contrast to α-chloroethylethyldichlorosilane, the α-carbonium ion formed in the case of an α-chloroethyltrichlorosilane reaction was only partially rearranged into a β-carbonium ion and as a result of the reaction α- and β-isomers were obtained in a ratio of 2.3 : 2 [1, 4].

TABLE 1

Substance	Frequencies (in cm^{-1})		
	1000 (meta-)	1030 (ortho-)	1090 (para-)
$C_2H_5Si(CH_3)CH_2CH_2C_6H_4Cl$	10	8	6
$(CH_3)_3SiCH_2CH_2C_6H_4Cl$	10	2	6

Aromatic compounds were also successfully silicoalkylated with chloromethylmethyldichlorosilane which, as is known, readily rearranges with $AlCl_3$ and without solvent into ethyltrichlorosilane. The reaction in this case proceeded only on heating and much more slowly than with α-chloroethylethyldichlorosilane, but still noticeably more rapidly than with chloromethyltrichlorosilane. Thus, substitution at the silicon atom of at least one chlorine atom by an alkyl radical activated the C–Cl bond in a silicoalkylation reaction.

In order to determine the relative position of the chlorine atom or the CH_3 group and the silicon-containing substituent in compounds produced by silicoalkylation of chlorobenzene and toluene we carried out spectral analyses of some of the substances obtained (which were first methylated).

We were able to determine approximately the ratios of the isomers, starting from the following premises: a) in Cl S spectra of monochloro substituted toluene [5] and other similar compounds, very intense symmetrical oscillations of the aromatic ring were observed at ~1000 cm^{-1} for the metal-substituted, at 1030-1040 cm^{-1} for the orthosubstituted and at 1090 cm^{-1} for the para-substituted derivatives; the intensities of these lines were approximately the same; b) an increase in the size of the substituting radical did not cause much change in the given characteristic frequencies; we checked these premises on specially synthesized p-ethylchlorobenzene. The relative intensities of the 1000, 1030 and 1090 cm^{-1} lines (in a scale of ten) are given in Table 1, whose data also show the approximate quantitative ratio of the isomers.

In the case of toluene derivatives, the spectra of compounds (I) and (II) were plotted.

$$C_2H_5Si(CH_3)CH_2CH_2C_6H_4CH_3 \quad \text{(I)} \qquad (CH_3)_3SiCH_2CH_2C_6H_4CH_3 \quad \text{(II)}$$

Some average values for the characteristic frequencies in CLS spectra of ortho-, meta- and para-benzene derivatives were given in one of the papers recently published [6]. An examination of the spectra of compounds (I) and (II) revealed the presence of frequencies 523-525, 725-730, 1000 (very intense) and 1250 cm^{-1}. This indicated that mainly meta-isomers were present. The weak frequencies observed in (I) and (II): 646, 780-830 and 1200 cm^{-1} indicated the presence of small amounts of the para-isomer. The absence of the 1220 cm^{-1} frequency and the very weak intensity of the 1040 cm^{-1} frequency made it impossible to establish the presence of ortho-derivatives.

EXPERIMENTAL

α- and β-chloroethylethyldichlorosilanes were prepared by chlorination of diethyldichlorosilane by the method in [7] and had the following properties.

α-Chloroethylethyldichlorosilane – b. p. 42-42.5° (10 mm), n_D^{20} 1.4570, d_4^{20} 1.2020.

β-Chloroethylethyldichlorosilane – b. p. 62° (10 mm), n_D^{20} 1.4669, d_4^{20} 1.2170.

TABLE 2

Silicoalkylating chloride	Aromatic compound	Compound obtained: formula	Compound obtained: name	Reaction mixture temperature	Reaction time (in hours)	Yield calculated on the starting chloride (in %)
CH_2SiCH_2Cl (Cl, Cl)	C_6H_5Cl	$CH_2SiCH_2C_6H_4Cl$ (Cl, Cl)	Chlorophenylmethylmethyldichlorosilane	120—130°	40	25.7
CH_2SiCH_2Cl (Cl, Cl)	$C_6H_5CH_3$	$CH_2SiCH_2C_6H_4CH_3$ (Cl, Cl)	Tolylmethylmethyldichlorosilane	120—125	60	15.8
$C_2H_5SiCHClCH_3$ (Cl, Cl)	C_6H_6	$C_2H_5SiCH_2CH_2C_6H_5$ (Cl, Cl) *	β-Phenylethylethyldichlorosilane	Room 30—40	20, 2—3	49.8
$C_2H_5SiCHClCH_3$ (Cl, Cl)	C_6H_5Cl	$C_2H_5SiCH_2CH_2C_6H_4Cl$ (Cl, Cl) *	β-Chlorophenylethylethyldichlorosilane	Room	25	24.8
$C_2H_5SiCHClCH_3$ (Cl, Cl)	$C_6H_4CH_3$	$C_2H_5SiCH_2CH_2C_6H_4CH_3$ (Cl, Cl) *	β-Tolylethylethyldichlorosilane	Room	70	24.6
$C_2H_5SiCH_2CH_2Cl$ (Cl, Cl)	C_6H_5Cl	$C_2H_5SiCH_2CH_2C_6H_4Cl$ (Cl, Cl) *	β-Chlorophenylethylethyldichlorosilane	20—45	2.5	41.5
$C_2H_5SiCH_2CH_2Cl$ (Cl, Cl)	$C_6H_4CH_3$	$C_2H_5SiCH_2CH_2C_6H_4CH_3$ (Cl, Cl) *	β-Tolylethylethyldichlorosilane	20—40	2.5	41.2

* These compounds were methylated with CH_3MgCl. The properties of the methylated obtained in experiments 4 and 6 and in 5 and 7, respectively, the properties of

TABLE 3

Substance obtained: Formula	Substance obtained: Name	Yield (in %)	Boiling point pressure, (in mm)	n_D^{20}
$C_2H_5SiCH_2CH_2C_6H_5$ (CH_3, CH_3)	β-Phenylethylethyldimethylsilane	82	226—227° (754)	1.4924
$C_2H_5SiCH_2CH_2C_6H_4Cl$ (CH_3, CH_3)	β-Chlorophenylethylethyldimethylsilane	73	117—118°(4)	1.5073
$C_2H_5SiCH_2CH_2C_6H_4CH_3$ * (CH_3, CH_3)	β-Tolylethylethyldimethylsilane	80	124—125 (15)	1.4934

* Sym.-dimethyldiethyl-di-(tolylethyl)-siloxane was also isolated, b. p. 211-213° (4 mm);

TABLE 2 (continued)

Boiling point, pressure (in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Empirical formula	Calc. (%) C	Calc. (%) H	Calc. (%) Si	Calc. (%) Cl	Found (%) C	Found (%) H	Found (%) Si	Found (%) Cl
118—119° (8)	1.5365	1.2763	58.62	58.19	$C_8H_9SiCl_3$	40.32	3.79	11.76	44.13	40.24, 40.12	3.75, 3.72	11.64, 11.58	43.75, 44.10
228—230 (754)	1.5189	1.1417	57.94	58.41	$C_9H_{12}SiCl_2$	49.52	5.50	12.85	32.13	49.44, 49.40	5.48, 5.46	12.69, 12.74	31.94, 31.82
130.2 (16)	1.5150	1.1122	62.90	62.80	$C_{10}H_{14}SiCl_2$	51.68	6.04	12.08	30.20	51.58, 51.64	6.02, 6.04	12.18, 12.24	30.12, 29.94
147 (10)	1.5288	1.2095	67.77	67.64	$C_{10}H_{13}SiCl_3$	45.06	4.88	10.52	39.54	44.90, 44.82	4.86, 4.84	10.60, 10.68	39.28, 39.14
269—270 (750)	1.5132	1.0941	67.64	67.43	$C_{11}H_{16}SiCl_2$	53.44	6.53	11.35	28.68	53.72, 53.80	6.76, 6.73	10.97, 10.95	27.58, 27.42
135—139 (8)	1.5287	1.2109	67.77	67.68	$C_{10}H_{13}SiCl_3$	45.06	4.88	10.52	39.54	44.80, 44.72	4.82, 4.82	10.32, 10.40	38.98, 39.14
121—123 (3)	1.5152	1.0967	67.64	67.43	$C_{11}H_{16}SiCl_2$	53.44	6.53	11.35	28.68	53.52, 53.64	6.50, 6.48	11.12, 11.04	28.10, 28.05

compounds are given in Table 3. As it was found that identical substances were methylated compounds obtained in experiments 3, 6 and 7 are given in Table 3.

TABLE 3 (continued)

d_4^{20}	MR_D found	MR_D calculated	Empirical formula	Found (%) C	Found (%) H	Found (%) Si	Calc. (%) C	Calc. (%) H	Calc. (%) Si
0.8724	63.77	63.78	$C_{12}H_{10}Si$	75.00	10.42	14.58	74.92, 74.96	10.38, 10.40	14.28, 14.36
0.9850	68.45	68.59	$C_{13}H_{19}SiCl$	63.60	8.42	12.34	63.71, 63.62	8.32, 8.57	11.74, 11.77
0.8767	68.33	68.17	$C_{13}H_{22}Si$	75.73	10.68	13.59	75.80, 75.69	10.59, 10.75	13.96, 13.47

$\overline{n_D^{20}}$ 1.5078, d_4^{20} 0.9453, MR_D 125.44; calc. 125.18.

Benzylmethyldichlorosilane. Chloromethylmethyldichlorosilane was reacted with benzene in a three-necked flask, fitted with a stirrer, a reflux condenser and a thermometer. In the flask was placed 65.3 g of chloromethylmethyldichlorosilane, 78 g of benzene and 3 g of $AlCl_3$. Evolution of hydrogen chloride began at the boiling point of the mixture (~90°). The mixture was boiled for 60 hours, with 1.5 and 2 g of $AlCl_3$ being added 15 and 30 hours after the beginning of the reaction. 60 hours after the beginning of the reaction there was almost no evolution of HCl. 12 g of $POCl_3$ and 30 ml of isooctane were added. The mixture was boiled for 1 hour and the $AlCl_3 \cdot POCl_3$ complex formed was filtered off. On distilling the filtrate we isolated 23.7 g of chloromethylmethyldichlorosilane and 21.0 g of benzylmethyldichlorosilane; the yield was 25.6% of the starting and 40% of the reacted chloromethylmethyldichlorosilane.

B. p. 214-215° (740), n_D^{20} 1.5210, d_4^{20} 1.1636, MR_D 53.78; calc. 53.38.

Found %: C 47.18, 47.05; H 5.13, 5.11; Cl 33.37, 33.75; Si 14.65, 14.64. $C_8H_{10}SiCl_2$. Calculated %: C 47.05; H 4.95; Si 13.81; Cl 34.15.

In addition we isolated 4.3 g of a crystalline substance with b. p. 299-302° (740 mm), m. p. 62° and corresponding in analysis to bis-(methyldichlorosilylmethyl)-benzene; the yield was 8.0%.

Found %: C 36.02, 36.08; H 4.23, 4.18; Si 17.08, 17.14; Cl 41.84, 41.98. $C_{10}H_{14}Si_2Cl_4$. Calculated %: C 36.40; H 4.24; Si 16.98; Cl 42.38.

The other silicoalkylations were carried out under conditions similar to those described above. The results are summarized in Table 2.

We obtained CLS (combination light scattering) spectra of phenylethylethyldimethylsilane and also of authentic β-phenylethylethyldimethylsilane, which was synthesized previously [1]. Comparison of the CLS spectra of the two compounds indicated their complete identity and the most characteristic frequency – fully symmetrical oscillation of the silicocarbon skeleton – had the value of 605 cm^{-1}, which is only 10 cm^{-1} below the analogous frequency of $(CH_3)_3SiCH_2CH_2C_6H_5$. A lowering of the frequency by ~10 cm^{-1} is also usually observed on substituting a CH_3 by a C_2H_5 group at the silicon atom. We must add that for $(CH_3)_3SiCH(CH_3)C_6H_5$, the analogous frequency appears at 625 cm^{-1}. The CLS spectra were obtained on an ISP-51 spectrography with a central cell by the usual method.

Reaction of β-chloroethylethyldichlorosilane with $AlCl_3$. Into a round-bottomed flask fitted with a reflux condenser was placed 47.5 g of β-chloroethylethyldichlorosilane and 1 g of $AlCl_3$ quickly added. A vigorous reaction occurred and the mixture boiled up. The mixture was then left at room temperature for 2 hours, the $AlCl_3$ filtered off and the filtrate distilled on a column. We isolated 38.5 g of ethyltrichlorosilane with b. p. 98° (755 mm), n_D^{20} 1.4235, d_4^{20} 1.2400; the yield was 95.3%.

Reaction of α-chloroethylethyldichlorosilane with $AlCl_3$. For the reaction we used 47.5 g of α-chloroethylethyldichlorosilane and 1 g of $AlCl_3$. The reaction was performed under the same conditions as in the previous experiment. From the distillation we obtained 35.3 g of ethyltrichlorosilane with b. p. 98-98.5° (733 mm), n_D^{20} 1.4233, d_4^{20} 1.2395; the yield was 87.4%.

SUMMARY

1. It was shown that chloroalkylalkyldichlorosilanes could be used successfully as silicoalkylating agents for aromatic compounds in the Friedel-Crafts reaction.

2. Silicoalkylation of benzene with α-chloroethylethyldichlorosilane gave only β-phenylethylethyldichlorosilane.

LITERATURE CITED

[1] A. D. Petrov, E. A. Chernyshev, M. E. Dolgaya, J. Gen. Chem. 25, 2469 (1955).*

[2] L. H. Sommer, D. L. Bailey, J. R. Gould, F. C. Whitmore, J. Am. Chem. Soc. 76, 861 (1954).

[3] L. H. Sommer, R. E. van Strein, F. C. Whitmore, J. Am. Chem. Soc. 71, 3056 (1949).

[4] G. H. Wagner, D. L. Bailey, A. H. Pines, Ind. Eng. Ch.. 45, 367 (1953).

*Original Russian pagination. See C. B. Translation.

[5] K. W. Kohlrausch, A. Pongratz, Monatsh. 63, 427 (1933).

[6] B. A. Kazansky, G. S. Landsberg, V. T. Aleksanyan, T. F. Bulanova et al., Bull. Acad. Sci. USSR, Phys. Series, 1954, 704.

[7] A. D. Petrov, V. A. Ponomarenko, L. L. Mkhitaryan, A. D. Snegova, Proc. Acad. Sci. USSR, 100, 1107 (1955).

Received August 15, 1956

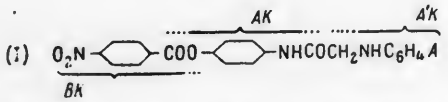
Institute of Organic Chemistry of the
Academy of Sciences USSR

COMPOUNDS WITH TWO ELECTRON DONOR SYSTEMS*

II. COLOR PHENOMENA IN DERIVATIVES OF N-(PHENYL-GLYCYL)-O--(3-NITROBENZOYL)-p-AMINOPHENOL

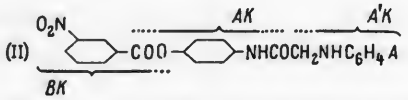
E. A. Smirnov

In the first report [1], which was devoted to an examination of compounds with two electron donor systems, we established that the derivatives of N-(phenyl-glycyl)-O-(4-nitrobenzoyl)-p-aminophenol of the general formula (I) are quite deeply colored: from orangish-red to dark cherry-red, although the electron donor systems in them, AK and A'K, are not connected by a conjugated double bond chain to the BK electrophilic system, which, from the point of view of the theory of conjugation, is essential for coloring [2].



A = H, CH_3, OCH_3 in ortho, meta and para positions.

In accordance with the hypothesis developed by us [3], the main reason for color in these compounds is the direct interaction of the electrophilic (BK) and electron donor (AK, A'K) chromophore systems involving exomolecular forces [4]. But, as the given compounds contain two separate electron donor systems, one might expect that the depth of color of the corresponding compound depended on which of the two systems the BK electrophilic system interacted with, as the "strengths" of the electron donor systems, AK and A'K, differ quite substantially. For compounds not containing an additional electron donor group (A = H), we could actually obtain two stably colored forms which differed quite strongly in depth of color: one was light red and the other was only light yellow. One might suppose that in the first case the relatively deep color of the compound was due to the interaction of the BK electrophilic system with the stronger A'K electron donor system and in the second case, the much lighter color was due to the interaction of the BK and AK systems. However, we could not obtain any of the other compounds of this series in a weakly colored form, whose existence could have been explained by the interaction of the BK and AK systems.** In order to extend our observations, we synthesized a series of preparations similar to those examined in the first report with the only difference that the NO_2 group in them was in a meta instead of a para position (II).



A = H, CH_3, OCH_3 in ortho, meta and para positions.

*Instead of "Compounds with two donorenoid systems" (see report I [1]), a simpler general title is given for the work here. An electron donor system is a system of double bonds with an electron donor group attached to it.

**A second, almost colorless form was obtained for the compound containing an m-OH group. However, the almost complete absence of visible color in this form would mean that no interaction occurred between the electrophilic and electron donor systems.

Color of Compounds with the General Formula

No. of substance	Substituting electron donor group (A)	Color of substance	
		in crystals	in powder
I	H	Pale yellow (b)	Pale yellow
II	o-CH_3	Orange (a)	Yellowish orange
III	m-CH_3	Brownish red (a)	Orangish red
		Pale yellow (b)	Greenish yellow
IV	p-CH_3	Intense yellow (a')	Bright yellow
V	o-OCH_3	Light red (a)	Pink
		Greenish yellow (b)	Greenish yellow (pale)
VI	m-OCH_3	Brownish red (a)	Brick red
VII	p-OCH_3	Red (a)	Orange-red
		Orange-yellow (a')	Orangish yellow

The compounds synthesized are listed in the table and the color of the substance in crystals and the powder form is given. As data in this table show, all the compounds in this series also are colored, the color reaching red and brownish red (compounds VII, III, VI). Some of these compounds could be obtained in two forms – one more deeply colored (a) and the other paler (b). Thus, the compound with the m-CH_3 group (III) had, besides a brownish red form, a pale yellow one; the two forms were quite stable and could be interconverted. The compound with the o-OCH_3 group (V) also gave two forms, very different in color. The compound with the p-OCH_3 (VII) also gave two forms; however in this case both forms had a deep color: red (a) and orange yellow (a'). The compound not containing an additional electron donor group (A = H) (I) was obtained only in a weakly colored form (pale yellow); in spite of all the attempts in this direction it could not be obtained in a more strongly colored form. The compound with a p-CH_3 group might be expected to give a red form, as usually, compounds containing electron donor groups in a position para to each other are colored somewhat more deeply than the corresponding ortho and meta isomers (Kauffmann's rule on the distribution of auxochromes [5]); in particular, this also occurs in the compounds described in report I. However, the given compound was obtained only as a quite intense yellow form, similar in color to the orangish yellow form of the compound with the p-OCH_3 group.

If one considers that the starting compound m-$O_2NC_6H_4COOC_6H_4NHCOCH_2Cl$ for the preparations in this series, which does not have an A'K electron donor system, is almost colorless, it is natural to assume that the quite deeply colored forms existing for almost all the compounds investigated are due to the presence of the A'K electron donor system in them. The latter, which includes a strong electron donor amino group in it, whose donor properties are not weakened as in the AK system, is a strong electron donor system in itself, regardless of the nature of the second electron donor group (A). Its interaction with the BK electrophilic system involving exomolecular forces causes the quite deep color of the corresponding compounds (forms a and a'). The presence of a second, weaker electron donor group (CH_3, OCH_3) in this system in various positions relative to the amino group increases, to a certain degree, its electron donor properties, which causes modifications in color for the various compounds in this series. If for comparison one took the more deeply colored forms of the compounds investigated, then the given groups could be arranged, according to their effect on the depth of color, in the following series: m-OCH_3 > m-CH_3 > p-OCH_3 > o-OCH_3 > o-CH_3 > p-CH_3 > H. It is noticeable that the most deeply colored compounds examined are those which contain an additional donor group (A) in a position meta to the NH, although, as is known, the para position of electron donor groups is usually the most favorable one for color. It is interesting to note that the red form of the compound containing the p-OCH_3 group is less deeply colored than the corresponding meta isomer, as well as the compound containing the weaker m-CH_3 electron donor group. The para derivatives in a series of analogous compounds with a p-NO_2 group [1] were most deeply colored and the electron donor groups could be arranged in a different order according to their effect on the depth of color: p-OCH_3 > p-CH_3 > o-OCH_3 > m-CH_3 > m-OCH_3 > o-CH_3 > H.

The existence of weakly colored forms (b) of compounds (I), (III) and (V) may be explained by the breakdown, in this case, of the interaction between the A'K electron donor and the BK electrophilic systems; the weak color of these forms was due to the interaction of the BK system with the considerably weaker AK electron donor system, both of whose electron donor groups are very much weakened by the addition of CO groups to them.

Without an AK system the breakdown of interaction between the BK and A'K systems should result in the disappearance of color from the corresponding compound (colorless form). We had observed these facts previously [6]; for example, the compound

$$p\text{-}O_2NC_6H_4CH_2CONHC_6H_4OH\text{-}m,$$

which has a light yellow color, may be isolated under certain conditions in a colorless form. The compounds

$$2,4\text{-}(O_2N)_2C_6H_3CH_2CH_2CONHC_6H_4N(CH_3)_2\text{-}m \text{ and}$$
$$2,4\text{-}(O_2N)_2C_6H_3CH_2CH_2CONHC_6H_4N(CH_3)_2\text{-}p$$

are also capable of giving a colorless form, besides the colored forms. Other authors [7, 8] have also made similar observations.

The presence of color in the weakly colored forms of compounds (I), (III) and (V) thus indicates that the AK system, in spite of its very weakened electron donor properties, is still capable of interacting with the BK electrophilic system. This is also indicated by the following facts: the compound $3,5\text{-}(O_2N)_2C_6H_3COOC_6H_4NHCOCH_2Cl$ (m. p. 185.5-186.5°), synthesized by us, which contains the same type of AK electron donor system but a stronger BK electrophilic system (two nitro groups), gives two forms, one of which is almost colorless and the other greenish-yellow. The presence of color in the latter may, apparently, be explained only by accepting the possibility of the AK system interacting with the BK system. If one accepts the possibility of the AK system interacting with the BK system, then one should assume that without a second electron donor group in the A'K system (A = H) (I) this A'K system interacts with the BK system with more difficulty than with the AK system, as compound (I) could only be obtained in a weakly colored form (light yellow). A similar picture is also observed for the corresponding compound with a nitro group in the para position. However, here we are able to isolate a deeply colored form (light red), but it formed with much greater difficulty than the weakly colored form (light yellow).

Regarding the two forms of the compound with the $p\text{-}OCH_3$ group, both of them are rather deeply colored and the lighter form cannot be explained by the interaction of the BK and AK systems. Both these forms arose, apparently, as a result of the interaction of the BK and A'K systems, and their difference must be due to peculiarities in the interaction of these systems.

According to Hantzsch's ideas [8], the existence of differently colored chromoisomers of homeopolarnitro compounds is due to the fact that the intracomplex bond between the NO_2 and the donor groups may be formed either with one or two oxygen atoms of the nitro group. However, from the point of view of contemporary electronic conceptions on complex bonds [9], such a hypothesis seems improbable. Kauffmann [10] explained the existence of the two chromoisomers (red and yellow) of 2,4-dimethoxy-4'-nitrostilbene that he prepared, as a polymorphous phenomenon, which seems more probable. It is possible that, in our case also, the existence of two colored forms (a and a') of compound (VII) produced by reacting the chromophorous systems BK and A'K is caused by a polymorphous phenomenon.

If one considers the hypothesis put forward by us explaining the existence of different colored forms of the compounds examined, then a satisfactory explanation may be given, for example, for the strong deepening of color on introducing even a weak electron donor group, such as CH_3, into compound (I): the compound changes from pale yellow to orange on introducing CH_3 groups in the ortho position and to brownish red on introducing the same groups in the meta position (III). Essentially different forms are compared here: form (b) of compound (I) with form (a) of compounds (II) and (III). However, in comparing the analogous forms (b) of compounds (I) and (III), we found that they were similarly colored (pale yellow). It is understandable also why the compound with the $p\text{-}CH_3$ group (IV) was one of the least deeply colored in the series of compounds investigated: the more deeply colored form of this compound, apparently, was not obtained and thus its less deeply colored form (a') was taken for comparison and compared with the more deeply colored form (a) of the other compounds. However, if this compound is compared with the analogous form (a') of compound (VII), the two of them appear very similar in

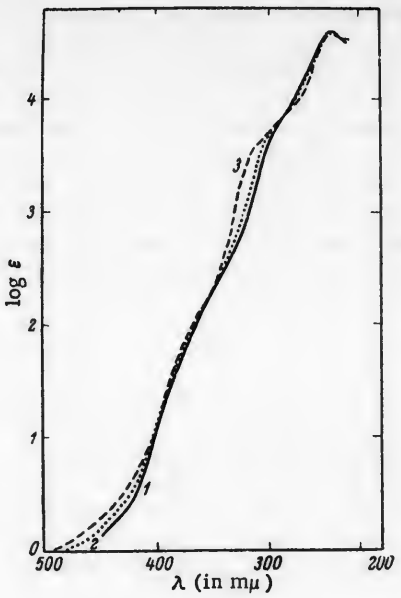


Fig. 1. Light absorption spectra of compounds of the type m-$O_2NC_6H_4COOC_6H_4NHCOCH_2NHC_6H_4A$. 1) A = H; 2) A = p-$CH_3$; 3) A = p-$OCH_3$.

color: intense yellow (IV) and orange-yellow (VII). The somewhat deeper color of the second compound corresponds fully to the stronger electron donor properties of the OCH_3 group in comparison with those of the CH_3 group.

It is, of course, more difficult to explain why a deeply colored form (a) could not be obtained for the compound with the p-CH_3 group, while it could be isolated quite readily for the compounds with the m-CH_3 and p-OCH_3 groups; it is also difficult to explain why only one deeply colored form could be obtained for the compound with the m-OCH_3 group, while two could be obtained for the compound with the p-OCH_3 group. Here, apparently, the individual properties of each compound appear and, primarily, those properties related to the steric distribution of electron donor groups.

Light absorption spectra. Considering that the absorption spectra of all the compounds described in the first report were very similar to each other, one would expect that in this case an analogous picture would be observed. We therefore limited ourselves this time to measuring the absorption spectra of only three compounds, namely: the compound not containing an additional electron donor group (I), the compound with the p-CH_3 group (IV) and the red form of the compound with the p-OCH_3 group (VII). As can be seen in Figure 1, the

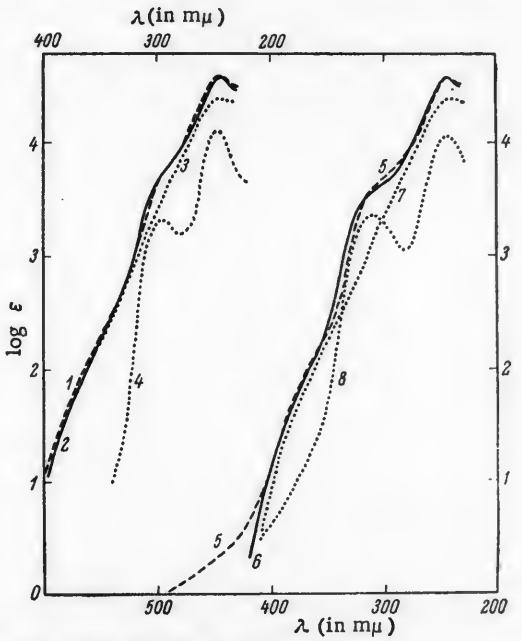


Fig. 2. Light absorption maxima.
1) m-$O_2NC_6H_4COOC_6H_4NHCOCH_2NHC_6H_5$; 2) total absorption curve for 3 and 4; 3) m-$O_2NC_6H_4COOC_6H_4NHCOCH_3$, 4) $C_6H_5CH_2NHC_2H_5$; 5) m-$O_2NC_6H_4COOC_6H_4NHCOCH_2NHC_6H_4OCH_3$-p; 6) total absorption curve for 7 and 8; 7) m-$O_2NC_6H_4COOC_6H_4NHCOCH_3$; 8) $C_6H_5CH_2NHC_6H_4OCH_3$-p.

absorption spectra of these three compounds were very similar both in form and in position, in spite of the fact that the color of the given compounds in the solid state differed considerably: the first was pale yellow, the second – intense yellow and the third – red. All the curves were characterized by a clearly expressed short wavelength maximum, whose position was practically the same for all three compounds (243-245 mμ). Furthermore, all the curves had a projection in the region of 290-310 mμ, corresponding to an absorption band with a maximum, whose position may be determined only approximately (~290 mμ). This projection was most noticeable for the compound with the p-OCH_3 group and least noticeable for the compound not containing an additional electron donor group (A = H). Finally, all the curves of the compounds investigated have also a third absorption band, situated in the visible region of the spectrum, also with an indistinctly expressed maximum (approximately at 410-420 mμ). Absorption in this region of the spectrum was characterized, however, by very small magnitudes which increased somewhat with increased donor properties of the additional electron donor group (A), i.e., in the order:

$$H < p\text{-}CH_3 < p\text{-}OCH_3.$$

Figure 2 gives curves plotted for the total absorption of two separate components, of which one ($C_6H_5CH_2NHC_6H_5$ or $C_6H_5CH_2NHC_6H_4OCH_3$-p) contained an electron donor system analogous to the A'K system and the second (m-$O_2NC_6H_4COOC_6H_4NHCOCH_3$) – BK and AK systems. The great similarity of these curves to the absorption curves of the compounds examined may be considered as proof that the main factor, on which the color of the given compounds in the solid state depends, namely the interaction between the systems BK and A'K, is to a great extent absent from the solution. The same figures give an idea as to the origin of both short wavelength maxima of the total curves and, consequently, of the corresponding compounds. The first, most clearly expressed maximum, appears as a result of the juxtaposition of the corresponding maxima of the separate components. The second, short wavelength maximum corresponds to the second maximum of the electron donor component (A'K). There is no absorption in the visible region of the spectrum of the total curves. This may indicate that the third absorption maximum, present in all the curves of the compounds examined and situated in the visible region of the spectrum results from the reaction of the electrophilic and electron donor systems. The very small absorption values, belonging to this section of the spectrum, indicate that these systems interact only to a very slight extent in the dilute solutions used for spectrum measurements.

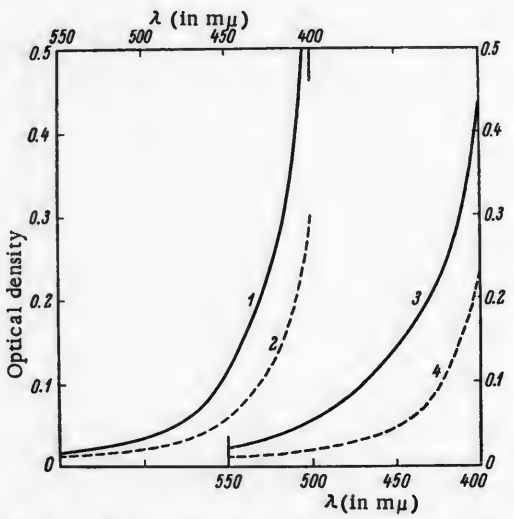


Fig. 3. Light absorption curves in pyridine solution.
1) m-$O_2NC_6H_4COOC_6H_4NHCOCH_2NHC_6H_4CH_3$-p ($2 \cdot 10^{-1}$ m, l = 0.1 cm); 2) the same ($4 \cdot 10^{-2}$ m, l = 0.5 cm); 3) m-$O_2NC_6H_4COOC_6H_4NHCOCH_2NHC_6H_4OCH_3$-p ($2 \cdot 1$)$^{-1}$ m, l = 0.1 cm); 4) the same ($2 \cdot 10^{-2}$ m, l = 1 cm).

It was natural to expect that at high concentrations of the solutions this interaction would occur to a greater extent, and this would lead to a deviation from Beer's law. In order to confirm this, we prepared considerably more concentrated pyridine solutions of two compounds: $2 \cdot 10^{-1}$ and $4 \cdot 10^{-2}$ m of compound (IV) and $2 \cdot 10^{-1}$ and $2 \cdot 10^{-2}$ M of compound (VII) and measured the visible region of their absorption spectra. The light absorption curves of these compounds are given in Figure 3. As can be seen from these figures, the curves corresponding to two different concentrations of the same compound are considerably displaced in relation to each other, although the products of concentration and thickness of layer of the solutions measured were equal and, consequently, if Beer's law applied in this case, the two curves should have coincided. This displacement was much greater for compound (VII) than for compound (IV) as in this case the $2 \cdot 10^{-1}$ M solution was diluted ten times while that of compound (IV) was diluted only five times. It is interesting to note that the $4 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ M solutions were only slightly yellowish although the compounds dissolved had a quite intense color in the solid state: the first was intense yellow, the second red. The $2 \cdot 10^{-1}$ M solutions had an intense yellow-orange color. The definite deviation from Beer's law may be considered to confirm the fact that the color of the compounds examined was caused by the existence of exomolecular interaction of the electrophilic and electron donor systems.

EXPERIMENTAL

N-(Chloroacetyl)-O-(3-nitrobenzoyl)-p-aminophenol. This was prepared from p-(N-chloroacetamino)-phenol (18.5 g) and m-nitrobenzoyl chloride (19 g) by the method we described previously for the preparation of the analogous compound with the nitro group in the para position [1]. The reaction product (21.5 g) was recrystallized from dilute (70%) acetic acid and then from methanol. We obtained almost colorless, prismatic crystals, as hemispherical nodules, with m. p. 157.5-158°. The preparation was readily soluble in acetone, dichloroethane and acetic acid, quite readily soluble in alcohol and methanol and difficultly soluble in benzene and ether.

Found %: Cl 10.56, 10.50. $C_{15}H_{11}O_5N_2Cl$. Calculated %: Cl 10.60.

N-(p-Tolyl-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (IV). A mixture of equal amounts (5 g each) of p-toluidine and the chloride (previous preparation), previously powdered and placed in a wide test tube, was heated for 15 minutes on a glycerin bath, when the temperature of the bath was quite quickly raised to 110° and then kept within the range 110-115°. The contents of the tube were stirred with a glass rod. At first everything melted and then crystallized as a compact mass with an orange-red color. 7-8 ml of methyl alcohol was added and the whole stirred. The precipitate became bright yellow. It was separated, washed with a small amount of methanol and recrystallized from dilute acetone (2 g of the precipitate was dissolved in 30 ml of acetone by heating, and 6 ml of hot water was added to the solution). The product was recrystallized a second time from methyl alcohol. The needle-like crystals obtained formed bright yellow radial nodules with m. p. 157.5-158°. The product was readily soluble in acetone, pyridine, chloroform and dichloroethane and quite readily soluble in methyl and ethyl alcohols and benzene. From all the solvents mentioned the substance separated as bright yellow crystals.

Found %: N 10.27. $C_{22}H_{19}O_5N_3$. Calculated %: N 10.36.

N-(m-Tolyl-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (III). The preparation of this and all the subsequent products was carried out similarly to the previous one, but the temperature and the time of heating were varied slightly. A mixture of m-toluidine and the chloride (2 g each) was heated for 30 minutes, when the temperature of the bath was gradually raised to 105°. After treatment with methyl alcohol, the red precipitate obtained was recrystallized from methanol (120 ml to 1.7 g of precipitate). Thus the product was obtained in the weakly colored form, which was pale yellow and had m. p. 141.0-141.5°. By recrystallization a second time from methanol, the red form was again obtained (slightly less methanol was taken this time: 56 ml to 1 g and 30-40 minutes heating was required for complete solution). The red form could be obtained by crystallization from pyridine with the addition of water. For this, the product (either in the yellow or red form) was dissolved in pyridine (10 ml of pyridine to 0.5 g of precipitate) and 2.5 ml of water was added to the hot solution. The red form crystallized as platelets, sometimes curved and agglomerated in nodules, in the form of brushes. On heating in a capillary to 122-125°, the red crystals changed into the yellow form, which melted at the temperature given above. As the pale yellow form, the substance readily separated from a mixture of methanol and acetone (1 : 1), forming narrow plates with sharp ends. Both forms were readily soluble in pyridine and acetone (even in the cold) and quite readily soluble in alcohol, benzene and methanol. Crystallization from alcohol and aqueous acetone gave a mixture of pale yellow and red crystals (the latter forming the minority).

Red form. Found %: N 10.51. $C_{22}H_{19}O_5N_3$. Calculated %: N 10.36.

Pale yellow form. Found %: N 10.41. $C_{22}H_{19}O_5N_3$. Calculated %: N 10.36.

N-(o-Tolyl-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (II). Heating was continued for 35 minutes. The initial bath temperature of 60° was raised to 125°. The mass crystallized on cooling and was dissolved in 10 ml of alcohol. To isolate crystals it was necessary to add a seed, otherwise the product could separate as an oil. The precipitate was recrystallized from alcohol, then from methanol and again from alcohol. We obtained brownish yellow crystals, which melted at 115-116° to form a turbid melt. On heating to 150°, the melt became clear and bubbles of gas were evolved. The product was readily soluble in acetone, alcohol, methanol, benzene and dichloroethane and dissolved even in the cold in the first.

Found %: N 10.47. $C_{22}H_{19}O_5N_3$. Calculated %: N 10.36.

N-(4-Methoxyphenyl-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (VII). Heating was continued for 15 minutes. The bath temperature was raised from 60° to 105°. The red precipitate, obtained after treatment with methanol, was recrystallized from methanol (200 ml of methanol to 2 g of precipitate). In the crystallization it was necessary to add a seed and allow the solution to cool gently. The red product obtained, with m. p. 140-141°, was readily soluble in acetone and dichloroethane (even in the cold in the first) and quite readily soluble in alcohol, methanol and benzene. On recrystallization from dilute acetone (2 : 1), the substance separated in the form of bright orange, prismatic crystals with m. p. 144-145° (1 g of the red substance was dissolved in 10 ml of acetone and 5 ml of water was added to the hot solution). On recrystallization from alcohol, the red form usually gave a mixture of both forms, but sometimes only the yellow. To prepare the red form from the yellow, the latter had to be dissolved in methanol (100 ml of methanol to 1 g of precipitate), a red seed added and the solution left to crystallize slowly. The red form could also be prepared by recrystallization from a mixture of acetone and methanol (3 : 2). However, in both cases a mixture of crystals of the yellow and red forms was sometimes isolated.

Red form. Found %: N 10.02. $C_{22}H_{19}O_6N_3$. Calculated %: N 9.98.

Yellow form. Found %: N 10.13. $C_{22}H_{19}O_6N_3$. Calculated %: N 9.98.

N-(2-Methoxyphenyl-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (V). A mixture of the starting materials (2 g each) was heated for 25 minutes. The bath temperature was raised to 120°. The red melt thus formed crystallized again during the heating. On adding methyl alcohol (10 ml) the red color disappeared and as a result we obtained a pale yellow precipitate. Part of the latter (1 g) was recrystallized from dilute acetone (the product was dissolved in 30 ml of acetone and 10 ml of water added to the hot solution). We obtained a pale greenish, flaky precipitate, containing a small amount of red crystals. The precipitate was recrystallized again from a mixture of acetone (25 ml) and water (10 ml). We obtained a homogeneous product with a pale greenish color and m. p. 154.5-155.3°. The other part of the precipitate, obtained after treatment with methyl alcohol, was recrystallized from a mixture of methanol (14 ml) and acetone (7 ml). The product obtained was in the form of red crystals with m. p. 157.5-158°. Both forms were readily soluble in acetone and pyridine and quite readily soluble in alcohol and benzene, though the red form was slightly less soluble in thelatter solvents than the yellow. They dissolved with considerably more difficulty in methyl alcohol than in ethyl. The substance separated from all the solvents in the weakly colored form, but sometimes with just a small amount of red crystals. It was possible to obtain the red form from methyl alcohol by slow crystallization and also from a mixture of methyl alcohol and acetone (2 : 1).

Pale greenish form. Found %: N 10.19. $C_{22}H_{19}O_6N_3$. Calculated %: N 9.98.

Red form. Found %: N 10.07. $C_{22}H_{19}O_6N_3$. Calculated %: N 9.98.

N-(Phenyl-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (I). A mixture of the chloride and aniline (2 g each) was heated for 25 minutes, while the temperature of the bath was raised to 105°. Again on heating, the mass first melted and then crystallized. 12 ml of methanol was added and the whole stirred. The solidified orange melt was converted into a pale yellow precipitate on treatment with methanol. The precipitate was recrystallized from dilute acetone (5 : 1) and then from methanol. The substance crystallized as narrow plates, sharp at the ends, with a pale yellow color and m. p. 193.5-194.0°. The product was readily soluble in pyridine, isoamyl alcohol and acetone, more difficultly soluble in alcohol and benzene and even more difficultly soluble in methanol. The substance separated from all the solvents in the weakly colored form. We were unable to obtain it in the more deeply colored form.

Found %: N 10.80. $C_{21}H_{17}O_5N_3$. Calculated %: N 10.74.

N-(3-Methoxy-glycyl)-O-(3-nitrobenzoyl)-p-aminophenol (VI). Heating was continued for 25 minutes. The maximum bath temperature was 105°. The brick-red precipitate obtained after treatment with methanol was recrystallized successively from methyl and ethyl alcohols. The product was isolated as brownish red crystals in hemispherical nodules. The m. p. was 123-124°. The product was readily soluble in acetone, dichloroethane and toluene and quite readily soluble in alcohol, methanol and benzene.

Found %: N 9.93. $C_{22}H_{19}O_6N_3$. Calculated %: N 9.98.

Spectroscopic measurements were carried out on a Beckmann spectrophotometer. As solvent we used rectified alcohol, previously distilled on a fractionating column. The concentrations used for the spectroscopic measurements of the alcohol solutions were 10^{-2}, 10^{-3} and 10^{-4} M. The visible part of the spectrum with more concentrated ($4 \cdot 10^{-1}$, $2 \cdot 10^{-1}$ and $2 \cdot 10^{-2}$ M) pyridine solutions was measured on an automatic recording SF-2 spectrophotometer with a layer thickness of 0.5 and 1.0 cm.

SUMMARY

1. We synthesized a series of compounds with two electron donor systems AK and A'K with the general formula (II). With the exception of the first (A=H), all the compounds synthesized were quite deeply colored: from intense yellow to brownish red.

2. The compounds with the m-CH_3 and o-OCH_3 groups could also be obtained in a weakly colored form (pale yellow and pale greenish-yellow color); the compound with the p-OCH_3 group was obtained in two relatively deeply colored forms: red and orange-yellow; the compound, not containing an additional donor group (A=H), was obtained only in a weakly colored form (pale yellow).

3. The color of the deeply colored forms of the compounds investigated was due to direct exomolecular interaction between the BK electrophilic and the A'K electron donor systems; the color of the weakly colored forms was due to reaction between the BK and AK systems.

4. We measured the light absorption spectra of three of the compounds synthesized (A = H, p-CH_3 and p-OCH_3). The absorption curves obtained were very similar to each other and to the absorption curves obtained for the total absorption of two components – one containing an electron donor system analogous to A'K ($C_6H_5CH_2NHC_6H_5$ or $C_6H_5CH_2NHC_6H_4OCH_3$) and the other containing the systems BK and AK (m-$O_2NC_6H_4COOC_6H_4NHCOCH_3$). This similarity was considered as proof that the main factor on which the color of the compounds examined in the solid state depended (direct reaction of the BK and A'K or AK systems), was to a great extent absent from the solution.

5. It was shown that at considerably greater solution concentrations of the given substances ($2 \cdot 10^{-1}$ and $2 \cdot 10^{-2}$ M) a noticeable deviation from Beer's law was observed. This was considered as proof that the main factor, affecting the color of these substances, was the interaction of electrophilic and electron donor systems involving exomolecular forces, and that this interaction was considerably disrupted in dilute solutions.

LITERATURE CITED

[1] E. A. Smirnov, J. Gen. Chem., Suppl. 11, 1394 (1953).

[2] A. Burawoy, Ber. 64, 142 (1931); G. N. Lewis and M. Calvin, Chem. Revs. 25, 273 (1934); Trans. Prog. Chem. 10, 43 (1941); Th. Förster, Z. Elektroch., 45, 548 (1939); Trans. Prog. Chem. 9, 100 (1940); W. R. Brode, Chemical Spectroscopy, 2, Ed. 224, 235 (1943).

[3] E. A. Smirnov, J. Gen. Chem. 20, 696 (1950);* 17, 309 (1947); 10, 1377 (1940); 10, 43 (1940); 25, 802, 1014, 2336, 2532 (1955);* see also: V. A. Izmailsky and E. A. Smirnov, J. Gen. Chem. 7, 513, 523 (1937); Proc. Acad. Sci. USSR, 20, 669 (1938); J. Gen. Chem. 25, 1400 (1955).*

[4] V. A. Izmailsky, Problems of the Aniline Dye Industry, Trans. VIII Conf. on Aniline Dye Chemistry and Techniques 8-11 December 1947, Bull. Acad. Sci. USSR, 88-117 (1950); V. A. Izmailsky and P. A. Solodkov, Proc. Acad. Sci. USSR, 60, 587 (1948).

[5] H. Kauffmann, Ber. 39, 2722 (1906); 44, 2386 (1911); 52, 1422 (1919); see also: V. A. Izmailsky and E. A. Smirnov, J. Gen. Chem. 7, 530 (1937).

* Original Russian pagination. See C. B. Translation.

[6] E. A. Smirnov, J. Gen. Chem. 17, 322 (1947).

[7] V. A. Izmailsky , D. K. Surkov, M. A. Volodina, J. Gen. Chem. 13, 841 (1943).

[8] A. Hantzsch, Lieb. Ann. 492, 65 (1931); Zbl. 1933, I, 2535; Abs. J., Chem. 4/7, 453 (1932).

[9] A. N. Terenin, Prog. Chem. 24, 153 (1955).

[10] H. Kauffmann, Ber. 54, 795 (1921).

Received September 17, 1956

Moscow Fuel Institute

THE REACTION OF ALKYLHALOSILANES WITH TRIALKYLSILANES

B. N. Dolgov, S. N. Borisov and M. G. Voronkov

In 1919 Stock and Somieski [1] obtained, for the first time, alkylsilanes of the type R_nSiH_{4-n} (n = 1,2) by reacting dimethylzinc with mono- and dichlorosilane. Due to the inaccessibility of halo- and dihalosilanes, they have only recently been used for the synthesis of alkylsilanes by Grignard's method [2, 3].* A more widely applied method has been the reduction of alkyl(aryl)chlorosilanes with lithium aluminum hydride [5].

$$4R_nSiCl_{4-n} + (4-n)LiAlH_4 \rightarrow 4R_nSiH_{4-n} + (4-n)(LiCl + AlCl_3) \quad (1)$$

By this method or modifications of it [6, 7] a series of new organosiiicon compounds were prepared containing Si—H bonds (alkyl- [5, 6], aryl- [8] and alkenylsilanes [9-11], silacyclanes [12-14] and disilylalkanes [14, 15]). Some alkyl- and dialkylsilanes could be prepared by adding SiH_4 or $RSiH_3$ (R — alkyl or aryl) to unsaturated organic compounds [16-19].

These methods of synthesizing alkyl- and dialkylsilanes are particularly difficult and require special equipment, while the starting materials are either difficult to obtain or highly explosive. However, alkyl- and dialkylsilanes are of considerable interest due to their specific chemical behavior (due to the presence of several Si—H bonds) and the profusion of isomeric forms. The latter are essential for elucidating the little-studied problem of the effect of the position of a silicon atom in a carbosilicon skeleton on the properties of alkylsilanes.

We recently described [20] a modification of the Whitmore reaction [21].

$$(C_2H_5)_2SiCl_2 + 2(C_2H_5)_3SiH \xrightarrow{AlCl_3} (C_2H_5)_2SiH_2 + 2(C_2H_5)_3SiCl \quad (2)$$

Investigation of this reaction showed that it is generally applicable and is a simple and rapid method for preparing alkylsilanes from alkylhalosilanes.

$$R_nSiX_{4-n} + (4-n)R'_3SiH \xrightarrow{AlCl_3} R_nSiH_{4-n} + (4-n)R'_3SiX$$

R and R′ —alkyls, and X = Cl, Br; $n = 1, 2$ (3)

The reaction proceeds on simple fractionation of the stoichiometric reagent mixture in the presence of catalytic amounts of $AlCl_3$ (Table 1) and under these conditions only alkylsilanes are produced and there are no partial reduction products.

Diethyldichloro- and dibromosilane** reduction with triethylsilane proceeded in full with a 55-60% yield of the very volatile diethylsilane and an almost quantitative yield of triethylchloro(bromo)silane. At first sight it seemed suprising that under analogous conditions there was no reaction between triethylsilane and diethyldiiodosilane. However, if one considers that alkyl iodides are considerably less reactive in reactions catalyzed by $AlCl_3$ than other alkyl halides [22, 23], then the inertness of the usually very active alkyliodosilanes is not suprising in this case. In comparison with $(C_2H_5)_2SiCl_2$, methylpropyldichlorosilane reacted with much greater difficulty with $(C_2H_5)_3SiH$ and was only 30-35% reduced in the presence of 1 mole % of $AlCl_3$. Increasing the amount of catalyst to 4 mole % resulted in 80% of the $CH_3(C_3H_7)SiH_2$ being converted into dialkylsilane. However, as a result of catalytic isomerization of the propyl radical, the reduction product was not the expected methyl-n-propylsilane,

* Besides halosilanes, $C_6H_5SiH_2Cl$ [4], prepared by a multistage synthesis, was used.

** The diethyldibromosilane was prepared by reacting diethylsilane with C_4H_9Br in the presence of $AlCl_3$. This reaction is a new and convenient method for preparing dialkyldibromosilanes, which were difficultly obtainable.

TABLE 1

The Reaction of Alkylhalosilanes With Triethylsilane in the Presence of $AlCl_3$

Alkylhalosilane	Molar ratio of reagents	$AlCl_3$ amount (mole %)	Alkylhalosilane conversion into alkylsilane (in %)	Reaction product yields*	
				alkylsilanes	triethylhalosilanes
$(C_2H_5)_2SiCl_2$	1 : 2	1.0	100	52.8	98.1
$(C_2H_5)_2SiBr_2$	1 : 2	1.5	100	59.2	89.4
$(C_2H_5)_2SiI_2$	1 : 2	3.0		—	—
$CH_3(n\text{-}C_3H_7)SiCl_2$ . . .	1 : 2	1.2	36.5	61.8	97.5
$CH_3(n\text{-}C_3H_7)SiCl_2$ . . .	1 : 2	4.0	81.3	47.0**	93.5
$n\text{-}C_4H_9SiCl_3$	1 : 3	2.0	90.0	98.0	93.9
$iso\text{-}C_4H_9SiCl_3$	1 : 3	1.3	76.9	98.2	96.8
$sec\text{-}C_4H_9SiCl_3$	1 : 3	1.4	72.3	97.5	94.2

* In percentages, calculated on reacted alkylhalosilane.

** Methylisopropylsilane.

TABLE 2

Properties of Isomeric Silapentanes

Compound	Boiling point	n_D^{20}	d_4^{20}	MR_D		H(—Si) (in %)	
				found	calculated	found	calculated
Methylisopropylsilane	49.4°	1.3790	0.6650	30.66	30.73	2.18, 2.24	2.28
Methylpropylsilane	53.6	1.3857	0.6738	30.74	30.73	2.14, 2.28	2.28
Diethylsilane	55.6	1.3916	0.6837	30.70	30.73	2.16, 2.21	2.28
Isobutylsilane	49.5	1.3890	0.6720	31.06	31.00	3.02, 3.08	3.43
Sec-butylsilane	49.3	1.3898	0.6738	31.02	31.00	3.08, 3.12	3.43
n-Butylsilane	54.1	1.3912	0.6756	31.04	31.00	3.23	3.43

but methylisopropylsilane, isomeric with it.*

Isomeric butyltrichlorosilanes reacted with triethylsilane in the presence of 1-2% of $AlCl_3$ to 70-90% with a quantitative yield of reaction products (calculated on reacted chlorosilane). On distilling $n\text{-}C_4H_9SiCl_3$ with $C_2H_5SiHCl_2$ in the presence of $AlCl_3$, no reduction occurred, which, without doubt, was due to the deactivating effect of the chlorine atom on the reactivity of the Si—H bond in ethyldichlorosilane.

Using reaction (3) we were able to synthesize and compare six isomeric silapentanes (Table 2), including sec.-butylsilane which has not been described in the literature.

We discussed previously [25] the mechanism of conjugated hydrogenation — halogenation (Equation (3)], caused by the transfer of the hydride-ion to the ionized complex of alkylhalosilane with $AlCl_3$.

EXPERIMENTAL

Starting materials. Triethylsilane was prepared in 60% yield by the reaction of C_2H_5MgBr with $C_2H_5SiHCl_2$ in a molar ratio of 2 : 1. The b. p. was 108.3°, n_D^{20} 1.4123, d_4^{20} 0.7316. n-Butyltrichlorosilane was prepared by

* It is interesting that isomerization of the propyl radical was not noted either in the disproportionation of $CH_3(C_3H_7)SiHCl$ in the presence of 8 mole % of $AlCl_3$ [20] or in the intermolecular radical exchange between $(C_2H_5)_4Si$ and $(C_3H_7)_4Si$, catalyzed by $AlCl_3$ [24].

treating n-C_4H_9MgBr with $SiCl_4$, in a ratio of 1 : 2 (yield 44.5%). Sec-butyltrichlorosilane (yield 61%) and isobutyltrichlorosilane (yield 64%) were prepared by the addition of silicochloroform to pseudo- or isobutylene, respectively, under pressure at 300° [26].

Methylpropyldichlorosilane was the product of the disproportionation of methylpropylchlorosilane in the presence of $AlCl_3$ [20].

Diethyldibromosilane. 35 g of butyl bromide was gradually added with cooling to a mixture, composed of 11.3 g of diethylsilane and 0.5 g of aluminum chloride in a round-bottomed flask, fitted with a reflux condenser and a thermometer. The reaction began at 4° and was complete after 3 hours, while the temperature of the reaction mixture was kept below 35°. A short period of heating was necessary to complete the reaction. From the reaction we obtained 5.38 liters of butane (93.1%) and 31.5 g of diethyldibromosilane with b. p. 164-167° (93.5%).

Diethyldiiodosilane. 63.5 g of powdered iodine was added with heating to a mixture of 68 g of diethyldiphenoxysilane* and 5.4 g of powdered aluminum. The reaction mixture was boiled under reflux until the violet color of the iodine disappeared. As a result of fractional distillation, we obtained 37.7 g of diethyldiiodosilane with b. p. 218-223° (44.4%).

TABLE 3

Properties of the Starting Alkylhalosilanes and Those Obtained

Compound	Boiling point	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Halogen content (in %) found	Halogen content (in %) calculated
Diethyldichlorosilane	128.2°	1.4307	1.0475	38.80	38.80	44.82, 44.92	45.13
Diethyldibromosilane	166.5	1.4857	1.5673	45.05	44.80	65.22, 65.63	64.96
Diethyldiiodosilane	221.2	1.5714	1.9711	56.71	55.77	73.74, 73.94	74.65
Methylpropyldichlorosilane	124.4	1.4250	1.0385	38.84	38.80	44.85, 45.07	45.13
Butyltrichlorosilane	145.5	1.4359	1.1610	43.14	43.06	55.43, 55.49	55.52
Isobutyltrichlorosilane	140.0	1.4381	1.1675	43.08	43.06	55.75, 55.90	55.52
Sec-Butyltrichlorosilane	144.0	1.4410	1.1766	43.00	43.06	55.80, 56.12	55.52
Triethylchlorosilane	146.8	1.4308	0.8885	43.89	43.80	22.76, 22.97	23.52
Triethylbromosilane	165.0	1.4570	1.1450	46.42	46.67	41.18, 41.45	40.94

The properties of the starting alkylhalosilanes and those obtained are given in Table 3.

The reaction of diethyldihalosilanes with triethylsilane.

a) The reduction of diethyldichlorosilane was described previously [20].

b) A mixture of 20.9 g of diethyldibromosilane, 19.8 g of triethylsilane and 0.5 g of aluminum chloride was distilled on a fractionation column with an efficiency of 20 theoretical plates. Thus we obtained 4.4 g of diethylsilane with b. p. 55-56° (59.2%) and 29.6 g of triethylbromosilane with b. p. 164-166° (89.4%). The starting materials reacted completely.

c) On fractionating a mixture of 29 g of diethyldiiodosilane, 19.8 g of triethylsilane and 1 g of aluminum chloride, we obtained only traces of unchanged starting materials.

The reaction of methyl-n-propyldichlorosilane with triethylsilane. a) On distilling a mixture of 23.5 g of methyl-n-propyldichlorosilane, 35 g of triethylsilane and 0.7 g of aluminum chloride on a fractionation column,

* This was prepared by heating diethyldichlorosilane with excess phenol until no more HCl was evolved. The b. p. was 301-303° (747.6 mm), n_D^{20} 1.5293, d_4^{20} 1.0433, MR_D 80.57; calc. 80.58. The yield was 82.3%. The product was characterized for the first time.

we obtained 3.0 g of methyl-n-propylsilane with b. p. 52-55° (61.8%), 22.2 g of unreacted triethylsilane (63.5% of the original). 14.7 g of unreacted methylpropyldichlorosilane (62.4% of the original) and 16.2 g of triethylchlorosilane with b. p. 144-147° (97.5%, calculated on the triethylsilane, which reacted). The conversion of the methylpropyldichlorosilane was 36.5%.

b) On fractionating a mixture of 20.6 g of methylpropyldichlorosilane, 30.6 g of triethylsilane and 2.1 g of aluminum chloride, we obtained 4.4 g of a product with b. p. 48-52°, n_D^{20} 1.3790, d_4^{20} 0.6650, which corresponded to methylisopropylsilane [20] (47%) and also 4.4 g of unreacted triethylsilane (14.3% of the original), 3.9 g of unreacted methylpropyldichlorosilane (18.7% of the original), 30.1 g of triethylchlorosilane (93.5%, calculated on the methylpropyldichlorosilane, which reacted) and 3.4 g of a product with b. p. 180-184°, n_D^{20} 1.4400 and % Cl 18.9, which was not examined more closely.

The reaction of butyltrichlorosilanes with triethylsilane. a) On distilling a mixture of 26.6 g of butyltrichlorosilane, 48.5 g of triethylsilane and 1.5 g of aluminum chloride on a fractionating column, we obtained fractions: 1st 52-56°, 10.8 g, (butylsilane); 2nd 56-143°, 2.2 g; 3rd 143-147°, 55.7 g (% Cl 25.0, which corresponds to a mixture containing 95.2% of triethylchlorosilane and 4.8% of butyltrichlorosilane); 4th above 147°, 6.1 g. 90% of the original butyltrichlorosilane reacted. The yield of butylsilane was 98% and of triethylchlorosilane 93.9% (calculated on the butyltrichlorosilane, which reacted).

b) On distilling a mixture of 6.4 g of isobutyltrichlorosilane, 11.7 g of triethylsilane and 0.23 g of aluminum chloride, we obtained fractions: 1st 49-51°, 2.2 g (isobutylsilane); 2nd 55-60°, 0.2 g (n_D^{20} 1.3915); 3rd 142-147°, 12.7 g (% Cl 27.2, which corresponds to a mixture containing 88.3% of triethylchlorosilane and 11.7% of butyltrichlorosilane); 4th above 147°, 1.8 g (n_D^{20} 1.4357) 76.9% of the original isobutyltrichlorosilane reacted. The yield of isobutylsilane was 98.2% and the triethylchlorosilane 96.8% (calculated on the isobutyltrichlorosilane, which reacted).

c) On fractionating a mixture of 10.3 g of sec-butyltrichlorosilane, 18.8 g of triethylsilane and 0.4 g of aluminum chloride, we obtained fractions: 1st 49-51°, 3.3 g (sec-butylsilane); 2nd 53-63°, 0.6 g (n_D^{20} 1.3913); 3rd 142-148°, 19.5 g (% Cl 28.15, which corresponds to a mixture containing 85.3% of triethylchlorosilane and 14.7% of sec-butyltrichlorosilane); 4th above 148°, 3.8 g (n_D^{20} 1.4421) 72.3% of the original sec-butyltrichlorosilane reacted. The yield of sec-butylsilane was 97.5% and of triethylchlorosilane 94.2% (calculated on the sec-butyltrichlorosilane, which reacted).

The reaction of n-butyltrichlorosilane with ethyldichlorosilane. On fractionating a mixture of 19.2 g of n-butyltrichlorosilane, 38.7 g of ethyldichlorosilane and 1 g of aluminum chloride, we obtained unchanged starting materials.

SUMMARY

1. The reaction of trialkylsilanes with alkylchloro(bromo)silanes, occurring in the presence of aluminum chloride, is a simple and rapid method of preparing alkyl- and dialkylsilanes. Under the conditions studied diethyldiiodosilane did not react with triethylsilane.

2. Depending on the amount of catalyst (aluminum chloride) used in the reduction of methyl-n-propyldichlorosilane with triethylsilane, either methyl-n-propylsilane or methylisopropylsilane is formed. Isomerization of the propyl radical at a silicon atom has not been observed previously.

3. Six isomeric silapentanes were prepared and among them sec-butylsilane which has not been described in the literature.

LITERATURE CITED

[1] A. Stock, C. Somieski, Ber. 52, 695 (1919).

[2] R. West, E. G. Rochow, J. Org. Ch. 1953, 303.

[3] H. E. Opitz, J. S. Peake, W. H. Nebergall, J. Am. Chem. Soc. 78, 292 (1956).

[4] M. C. Harvey, W. H. Nebergall, J. S. Peake, J. Am. Chem. Soc. 76, 4555 (1954).

[5] A. E. Finholt, A. C. Bond, K. E. Wilzbach, H. I. Schlesinger, J. Am. Chem. Soc. 69, 2108 (1947).

[6] H. Westermark, Acta Chem. Scand. 8, 1830 (1954); 9, 947 (1955).

[7] N. C. Goodspead, R. T. Sanderson, J. Inorg. Nuclear. Chem. 2, 266 (1956).

[8] R. A. Benkeser, H. Landesman, D. J. Foster, J. Am. Chem. Soc. 74, 648 (1952).

[9] S. Tannenbaum, S. Kaye, G. F. Lewenz, J. Am. Chem. Soc. 75, 3753 (1953).

[10] V. A. Ponomarenko, V. F. Mironov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 497.*

[11] A. D. Petrov, V. A. Ponomarenko, V. I. Boikov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, 504.*

[12] A. D. Plate, N. A. Momma, Yu. P. Egorov, Proc. Acad. Sci. USSR, 97, 847 (1954).

[13] R. West, J. Am. Chem. Soc. 76, 6012 (1954).

[14] A. D. Petrov, V. A. Ponomarenko, Proc. Acad. Sci. USSR, 90, 387 (1953).

[15] W. D. English, A. Taurins, R. V. V. Nickolls, Canad. J. Chem. 30, 646 (1952)

[16] G. Fritz, H. Kautsky, Z. Naturforsch., 5B, 395 (1950); 7B, 207 (1952); British Pat. 730379 (1955); Ch. A. 49, 12875 (1955).

[17] U. S. Pat. 2537763 (1951); Ch. A, 45, 3409 (1951).

[18] D. G. White, E. G. Rochow, J. Am. Chem. Soc. 76, 3897 (1954).

[19] J. Speier, R. Zimmerman, J. Webster, J. Am. Chem. Soc. 78, 2278 (1956).

[20] B. N. Dolgov, S. N. Borisov, M. G. Voronkov, J. Gen. Chem. 27, 2062 (1957).*

[21] F. C. Whitmore, E. W. Pietrusza, L. H. Sommer, J. Am. Chem. Soc. 69, 2108 (1947).

[22] C. Friedel, J. Crafts, Ann. Chem. (6), 1, 455 (1884).

[23] N. O. Calloway, J. Am. Chem. Soc. 59, 1474 (1937).

[24] P. D. George, L. H. Sommer, F. C. Whitmore, J. Am. Chem. Soc. 77, 1677 (1955).

[25] B. N. Dolgov, M. G. Voronkov, S. N. Borisov, J. Gen. Chem. 27, 709 (1957).*

[26] V. A. Kolesova, M. G. Voronkov, Coll. Czech. Chem. Papers, 22, 851 (1957).

Received October 31, 1956

Leningrad State University and Institute
of Silicate Chemistry of the
Academy of Sciences USSR

*Original Russian pagination. See C. B. Translation.

CATALYTIC ALKYLATION OF PHENOL WITH METHYL ALCOHOL

I. N. Samsonova

A series of papers [1-8] has been devoted to the catalytic alkylation of phenol with secondary and tertiary alcohols. Attempts at catalytic alkylation of phenol with primary alcohols gave negative results [2, 3, 9] or very low yields [10-13]. In the alkylation of phenol with methyl alcohol, the best results were obtained on activated aluminum oxide [14].

We studied the process of alkylating phenol with methyl alcohol over an activated natural aluminosilicate catalyst – gumbrine clay – at atmospheric pressure in the apparatus usually used for investigating vapor phase catalytic reactions in a circulating system. Liquid and gaseous products were obtained as a result of the reaction. The liquid, two-layer condensate contained, besides the unreacted starting substances, water, alkylated phenols and neutral reaction products.

In order to elucidate the relation of alkylated product yield to the temperature, the condensate was collected for analysis at three temperatures (350, 420 and 500°), with a molar ratio of phenol and methyl alcohol of 1 : 6 and a starting mixture input rate equal to 8-10 ml per hour over 100 ml of catalyst. On increasing the reaction temperature from 350 to 500°, the alkylated phenol yield increased almost three-fold and was 68% (calculated on the condensate phenols). The optimal yield of neutral condensation products was obtained at 420° and was 23% (calculated on total condensate).

The alkylated phenols, obtained at the three given temperatures, were a mixture of phenol derivatives containing cresols, xylenols and more complex products. The amount of the latter increased noticeably on increasing the reaction temperature. The mixture of alkylated phenols, obtained at 350°, contained 32% of o-cresol. The presence of o- and m-cresols was established in the alkylation products obtained at 420°. Very little o-cresol and 3,5-dimethylphenol were isolated from the phenol part of the condensate, obtained at 500°. The bulk of the phenols obtained at this temperature consisted of high-boiling, complex alkylation products.

Besides alcohol and water, anisole, o-methylanisole and hexamethylbenzene were detected in the neutral part of the condensate. The greatest amount of anisole (60.8% calculated on the neutral oil) was obtained at 420°. The maximum hexamethylbenzene yield (14%) was obtained at 500°. The amount of o-methylanisole was insignificant in all cases.

EXPERIMENTAL

As a result of catalytic condensation of phenol with methyl alcohol over hydrochloric acid-activated gumbrine clay, we obtained a two-layer condensate. The aqueous and oily layers were separated and from each layer a product was distilled boiling at up to 100°. The oily residue, boiling above 100°, was extracted several times with 10% NaOH. The phenolates obtained were extracted with ether to remove the neutral oils, which had been carried along with the alkali, and decomposed with dilute H_2SO_4.

After drying the ether solution and evaporating off the ether, we obtained a mixture of phenols, which was then fractionated. Up to 182°, unreacted phenol distilled off. Then the derivatives of phenol were fractionated on a column. The phenols were analyzed by arylization [15]. The crystalline aryiglycollic acids obtained were separated by fractional crystallization.

During operation it was established that after 18 hours' operation the catalyst lost 30% of its activity. This deactivation of the catalyst was probably caused by the deposition of tar and carbon on its surface, as a result of which the surface became difficultly accessible to the reagents. During all the experiments, the catalyst was

regenerated by blowing air through the reaction tube at a temperature of 350°, after 6 hours operation. After 18 hours operation, a fresh portion of catalyst was placed in the reaction tube.

Freshly distilled, dried phenol and distilled methyl alcohol were used as starting materials.

Alkylation at 350°. Starting mixture: 365.4 g of phenol, 746 g of methyl alcohol. After separating off the neutral products and the unchanged phenol, we obtained 38 g of a phenolic product with b. p. 182-210° and 159 g of a neutral oil, boiling in the range 152-250°. As a result of fractionation on a column, we isolated from the phenolic mixture 11.5 g of a fraction with b. p. 187-189°. The arylglycollic acid obtained from part of the fraction had m. p. 151-152° after recrystallization, which corresponds to the melting point of o-cresoxyacetic acid (according to literature data, 152°).

From the neutral oil we isolated:

1) Anisole (48.5 g): b. p. 155°, n_D^{20} 1.5162, d_4^{20} 0.9884.

Found: M 108, 109.5. C_7H_8O. Calculated M 108.

2) o-Methylanisole (11 g): b. p. 170-172°, n_D^{20} 1.5190, d_4^{20} 0.9850.

Found: M 122, 125. $C_8H_{10}O$. Calculated: M 122.

3) Hexamethylbenzene (4.8 g) – long needles with m. p. 164-166° (according to literature data, 166°).

Found: M 161, 165. $C_{12}H_{18}$. Calculated: M 162.

The gaseous reaction products contained 12.4% H_2, 32% CO_2, 10.8% CO, 9.2% C_nH_{2n}.

Alkylation at 420°. Starting mixture: 305 g of phenol, 623 g of methyl alcohol. After separation of the neutral products and the unchanged phenol, we obtained 36 g of a phenolic mixture with b. p. 182-224°. As a result of fractionation of the mixture, we isolated two fractions, which were shown to contain isomeric cresols. The fraction 189-191° (6 g) contained o-cresol. The melting point of the arylglycollic acid obtained was 151-152° (according to literature data, 152°). The fraction 200-203° (2.8 g) contained m-cresol. The melting point of the arylglycollic acid was 100-103°, which corresponds to the melting point of m-cresoxyacetic acid (according to literature data, 103°).

Investigation of the neutral oil (128 g) showed that it contained anisole (62 g), o-methylanisole (7.5 g) and hexamethylbenzene (7 g).

Alkylation at 500°. Starting mixtures: 305 g of phenol, 623 g of methyl alcohol. After preliminary treatment of the condensate, we obtained 105.5 g of a mixture of alkylated derivatives of phenol with b. p. 182-233° and 12 g of phenols with b. p. above 233°. As a result of analysis of the phenolic mixture, we established that it contained an insignificant amount of o-cresol (melting point of the o-cresoxyacetic acid obtained, 151-152°) and 3,5-dimethylphenol (melting point of the arylglycollic acid obtained, 84-86°).

The neutral oil (88 g) contained anisole (28.5 g), o-methylanisole (7 g) and hexamethylbenzene (14.2 g).

SUMMARY

A mixture of methyl alcohol with phenol over a natural aluminosilicate catalyst, gumbrine clay, at 320-500° gave alkylated phenol derivatives and neutral products. We isolated o- and m-cresol and 3,5-dimethylphenol. The neutral reaction products contained anisole, o-methylanisole and hexamethylbenzene.

LITERATURE CITED

[1] F. Fischer, Grützner, Ber. 26, 1646 (1893).

[2] A Chichibabin, Bull. Acad. Sci. USSR, VII ser., 951 (1935).

[3] H. Meyer, K. Bernhauer, Monatsh. 53-54, 721 (1929).

[4] J. Sears, J. Org. Ch. 13, 120 (1948).

[5] I. Tsukervanik, Z. Nazarova, J. Gen. Chem. 5, 767 (1935).

[6] R. Huston, M. Hsieh, J. Am. Chem. Soc. 58, 439 (1936).

[7] R. Huston, Langdon, Snyder, J. Am. Chem. Soc. 70, 1474 (1948).

[8] I. Tsukervanik, V. Tambovtseva, J. Gen. Chem. 15, 820 (1945).

[9] A. Liebmann, Ber. 14, 1842 (1881); 15, 150, 547 (1892).

[10] H. Auer, Ber. 17, 670 (1884).

[11] Briner, Pluss, Paillard, Ch. A., 19, 2648 (1925).

[12] V. N. Ipatyev, N. A. Orlov, A. D. Petrov, J. Russ. Phys. Chem. Soc., 59, 181, 541 (1927).

[13] O. Hinsberg, Zbl., 1932, I, 2094.

[14] N. Cullinane, Chard, J. Chem. Soc., 1945, 821.

[15] Holzman, Pilat, Brenn. Ch., 20, 403 (1930).

Received October 30, 1956

Leningrad State University

SYNTHESIS OF AROMATIC COMPOUNDS OF ANTIMONY

IX. PREPARATION OF ANTIMONIOAROMATIC COMPOUNDS USING ANTIMONY PENTACHLORIDE AND PHENYLHYDRAZINE

A. B. Bruker

In previous reports [1] we described a new method of preparing aromatic compounds of antimony, which consisted of reacting an arylhydrazine with antimony trichloride in the presence of cupric chloride and aerobic oxygen.

The purpose of the present work was to check the possibility of preparing aromatic compounds of antimony by reacting an arylhydrazine hydrochloride with antimony pentachloride. O. A. Reutov [2] synthesized double diazonium salts of antimony pentachloride by the exchange reaction

$$ArN_2Cl \cdot FeCl_3 + SbCl_5 \rightarrow ArN_2Cl \cdot SbCl_5 + FeCl_3$$

and used them for synthesizing various organoantimony compounds of pentavalent antimony by decomposing these salts in acetone with cuprous chloride or iron powder. The reaction between phenylhydrazine and antimony pentachloride was carried out under conditions analogous to those for preparing phenyl- and diphenylantimonic acids by reacting phenylhydrazine with antimony trichloride. Reaction of phenylhydrazine with antimony pentachloride in hydrochloric acid in the presence of cupric chloride gave a precipitate. Treatment of this precipitate with hot dilute hydrochloric acid gave diphenylstibine trichloride, which was reduced with sulfur dioxide to diphenylstibine chloride. The process of antimonioaromatic compound formation using antimony pentachloride may be described as follows: phenylhydrazine hydrochloride is oxidized by aerobic oxygen in the presence of cupric chloride to phenyldiazonium chloride; the latter gives a binary compound with antimony pentachloride

$$C_6H_5NHNH_2 \cdot HCl + SbCl_5 + O_2 \xrightarrow{CuCl_2} C_6H_5N_2Cl \cdot SbCl_5 + 2H_2O$$

This binary compound reacts with the phenylhydrazine hydrochloride in the reaction to give phenyldichlorostibine, which reacts with phenyldiazonium chloride to form the binary compound $C_6H_5N_2Cl \cdot C_6H_5SbCl_2$. Decompositions of this compound with hydrochloric acid gives diphenylstibine trichloride.

$$C_6H_5NHNH_2HCl + C_6H_5N_2Cl \cdot SbCl_5 \xrightarrow{CuCl_2} C_6H_5SbCl_2 + C_6H_5N_2Cl + N_2 + 4HCl$$
$$C_6H_5N_2Cl + C_6H_5SbCl_2 \rightarrow C_6H_5N_2Cl \cdot C_6H_5SbCl_2 \rightarrow (C_6H_5)_2SbCl_3 + N_2$$

This is confirmed by the following facts, observed in this work. The binary compound $C_6H_5N_2Cl \cdot C_6H_5SbCl_2$ was isolated both in the reaction of phenylhydrazine hydrochloride with antimony pentachloride in hydrochloric acid in the presence of cupric chloride and aerobic oxygen and in the reaction of phenylhydrazine hydrochloride with antimony pentachloride and phenyldiazonium chloride in hydrochloric acid in the presence of cupric chloride.

In order to prove that the binary compound $C_6H_5N_2Cl \cdot SbCl_5$ was an intermediate in this reaction, we synthesized this binary compound from phenyldiazonium chloride and antimony pentachloride in hydrochloric

acid. By reacting this binary compound with phenylhydrazine in hydrochloric acid in the presence of cupric chloride we obtained diphenylstibine trichloride.

At the same time, it was established that if phenylhydrazine hydrochloride was reacted with antimony pentachloride in the presence of cupric chloride without letting in aerobic oxygen, then the antimonioaromatic compound did not form. However, by reacting the binary compound $C_6H_5N_2Cl \cdot SbCl_5$ with phenylhydrazine hydrochloride in the presence of cupric chloride, the antimonioaromatic compound formed even without aerobic oxygen. If these reactions were carried out with aerobic oxygen but without the catalyst ($CuCl_2$), the antimonioaromatic compound did not form in either case. Thus, the synthesis of antimonioaromatic compounds by reacting phenylhydrazine hydrochloride and antimony pentachloride in hydrochloric acid in the presence of cupric chloride and aerobic oxygen may be expressed by the following reactions

$$C_6H_5NHNH_2 \cdot HCl + O_2 \xrightarrow{CuCl_2} C_6H_5N_2Cl + 2H_2O$$

$$C_6H_5N_2Cl + SbCl_5 \rightarrow C_6H_5N_2Cl \cdot SbCl_5$$

$$C_6H_5N_2Cl \cdot SbCl_5 + C_6H_5NHNH_2 \cdot HCl \xrightarrow{CuCl_2} C_6H_5N_2Cl + C_6H_5SbCl_2 + N_2 + 4HCl$$

$$C_6H_5N_2Cl + C_6H_5SbCl_2 \rightarrow C_6H_5N_2Cl \cdot C_6H_5SbCl_2 \rightarrow (C_6H_5)_2SbCl_3 + N_2$$

EXPERIMENTAL

Reaction of phenylhydrazine hydrochloride with antimony pentachloride in hydrochloric acid in thepresence of catalysts

a) Preparation of a precipitate of the binary compound $C_6H_5N_2Cl \cdot C_6H_5SbCl_2$. Into an open jar was placed water (240 ml) and concentrated hydrochloric acid (120 ml); to this we gradually added, with stirring, antimony pentachloride (30 g), then ferric chloride (3.5 g) and phenylhydrazine hydrochloride (29 g) and after 15-20 minutes, a solution of cupric chloride [0.3 g in 10 ml of hydrochloric acid (1 : 2)]. After 50 hours stirring (over a period of 8 days) the slightly yellowish precipitate formed was separated off, washed with dilute hydrochloric acid (1 : 2), alcohol and ether, and dried in air. The weight of the product was 40 g. The slightly yellowish powder, with no odor, gave a diazo reaction with β-naphthol and was insoluble in most organic solvents; in acetone it decomposed with the evolution of nitrogen. On boiling with dilute hydrochloric acid, the precipitate gave diphenylstibine trichloride (I).

Found %: Cl 25.73. $C_{12}H_{10}N_2Cl_3Sb$. Calculated %: Cl 25.96.

b) Preparation of (I). 40 g of the precipitate obtained was decomposed by heating with 500 ml of dilute hydrochloric acid; nitrogen was evolved and a small amount of oil formed. On separating off the oil and cooling the filtrate, a product crystallized out with m. p. 173° (after a second recrystallization). The yield was 18 g (45%, calculated on the antimony pentachloride).

Found %: Cl 25.9; Sb 30.82. $C_{12}H_{10}Cl_3Sb \cdot H_2O$. Calculated %: Cl 26.58; Sb 30.43.

c) Preparation of diphenylchlorostibine from (I). 5 g of (I) was dissolved in 125 ml of dilute hydrochloric acid (1 : 2) by heating, 15 ml of ethyl alcohol added and the whole filtered.* 1-2 crystals of potassium iodide were added and a stream of sulfur dioxide was passed through for 40-60 minutes. After cooling and partial evaporation of the alcohol, crystals of diphenylchlorostibine precipitated.** The yield was 3 g (77%). The colorless plates with m. p. 69-70° were readily soluble in alcohol, ether and acetone.

Found %: Sb 39.00. $C_{12}H_{10}ClSb$. Calculated %: Sb 39.12.

Reaction of phenylhydrazine hydrochloride, antimony pentachloride and phenyldiazonium chloride in hydrochloride in the presence of copper salts

a) Preparation of phenyldiazonium chloride. A solution of aniline hydrochloride (32.5 g of aniline in 85 ml of concentrated hydrochloric acid) was cooled and stirred and diazotized with a saturated solution of

* On the separation of an oil, alcohol was added until the oil completely dissolved.

** After separation of the diphenylchlorostibine, it was possible to obtain a further small amount of product from the mother liquor by distilling off the alcohol in vacuum.

sodium nitrate (24.2 g) until it gave a reaction with starch-iodide paper.

b) Preparation of precipitate. A solution of phenyldiazonium chloride, cooled to −5°, was gradually added over a period of 4 hours under the level of the liquid to a solution containing antimony pentachloride (74.9 g), phenylhydrazine hydrochloride (38 g), cupric chloride (2 g) and hydrochloric acid (750 ml, 5.8%). After the addition of the phenyldiazonium chloride, the mixture obtained was stirred for a further 2 hours. The precipitate formed was separated off and washed several times with dilute hydrochloric acid, alcohol and ether. After drying in air, the precipitate weighed 72.2 g (70.3%, calculated on the antimony pentachloride).

Found %: N 7.04; Sb 28.9; Cl 25.8. $C_{12}H_{10}N_2Cl_3Sb$. Calculated %: N 6.83; Sb 29.68; Cl 25.96.

The binary compound $C_6H_5N_2Cl \cdot C_6H_5SbCl_2$ was converted to (I) by heating with dilute hydrochloric acid.

Reaction of phenyldiazonium chloride with antimony pentachloride

A solution of aniline hydrochloride (10 g of aniline and 40 ml of hydrochloric acid) was cooled and stirred and diazotized with a solution of sodium nitrite (8 g). At the end of the diazotization, antimony pentachloride (30 g) was poured in dropwise with stirring at a temperature of 0-2°. The precipitate formed after some time was separated off and washed with dilute hydrochloric acid and ether. The yield was 43 g (97%, calculated on the antimony pentachloride). The almost colorless powder melted with decomposition at 85°, was slightly soluble in alcohol and ether and gave a diazo reaction with β-naphthol.

Found %: Sb 27.80. $C_6H_5N_2Cl_6Sb$. Calculated %: Sb 27.0.

Reaction of phenylhydrazine hydrochloride with the binary compound $C_6H_5N_2Cl \cdot SbCl_5$ (II) in hydrochloric acid in the presence of catalysts

Into an open jar was placed hydrochloric acid (120 ml) and water (240 ml), followed by the binary compound (II) (44 g), phenylhydrazine hydrochloride (15 g) and ferric chloride (3 g). After 15-20 minutes a solution of cupric chloride (0.3 g) in 10 ml of dilute hydrochloric acid was added. The precipitate, formed after 18 hours stirring, was separated off from the liquid, washed with dilute hydrochloric acid and decomposed by boiling with 500 ml of dilute hydrochloric acid (1 : 2). After separating off the oil and cooling the filtrate, we obtained 6.5 g (16%) of crystals of (I). After a second recrystallization, the m. p. was 172°.

Found %: Cl 25.41; Sb 30.39. $C_{12}H_{10}Cl_3Sb \cdot H_2O$. Calculated %: Cl 26.58; Sb 30.43.

Reaction of phenylhydrazine hydrochloride with antimony pentachloride in hydrochloric acid in the presence of catalysts without access to air

Into a closed jar with a stirrer was placed hydrochloric acid (360 ml, 1 : 2), antimony pentachloride (30 g), phenylhydrazine (22 g) and ferric chloride (3 g). After 15-20 minutes, a solution of cupric chloride (0.3 g) in 10 ml of hydrochloric acid (1 : 2) was added. After 200 hours stirring (over a period of 33 days), the precipitate was separated from the liquid. The weight of the precipitate (phenylhydrazine hydrochloride) was 20 g after recrystallization. The precipitate did not melt up to 200°. From the filtrate we isolated 9 g of inorganic antimony. We were unable to isolate organoantimony compounds.

Reaction of the binary compound (II) with phenylhydrazine hydrochloride in the presence of catalysts without excess to air

Into a closed jar, fitted with a stirrer with a mercury seal, was placed hydrochloric acid (360 ml, 1 : 2), the binary compound (II) (44 g), phenylhydrazine hydrochloride (15 g) and ferric chloride (3 g). After 15-20 minutes a solution of cupric chloride (0.3 g) in 10 ml of hydrochloric acid (1 : 2) was added. After 20 hours stirring, the precipitate obtained (24 g) was decomposed by boiling with dilute hydrochloric acid. The yield of (I) was 6 g (15%, calculated on antimony pentachloride). The m. p. was 172°.

Found %: Cl 25.8; Sb 30.49. $C_{12}H_{10}Cl_3Sb \cdot H_2O$. Calculated %: Cl 26.58; Sb 30.43.

Reaction of phenylhydrazine hydrochloride and antimony pentachloride in hydrochloric acid in the absence of catalysts

From a reaction mixture composed of phenylhydrazine (22 g), antimony pentachloride (30 g) and dilute hydrochloric acid (360 ml, 1 : 2), we recovered the starting materials after 280 hours stirring (over a period of 47 days). We were unable to isolate antimonioaromatic compounds.

Reaction of the binary compound (II) with phenylhydrazine hydrochloride in the absence of catalysts

After 70 hours stirring in a closed vessel, we recovered the starting materials from the reaction mixture. We were unable to isolate antimonioaromatic compounds.

SUMMARY

We developed a new method for preparing antimonioaromatic compounds, which consists of reacting phenylhydrazine hydrochloride and antimony pentachloride in a hydrochloric acid solution in the presence of cupric chloride. Ideas on the mechanism of this reaction were put forward.

LITERATURE CITED

[1] P. G. Sergeev, A. B. Bruker, J. Gen. Chem. 27, 2220 (1957);* A. B. Bruker, J. Gen. Chem. 27, 2223 (1957);* A. B. Bruker, J. Gen. Chem. 27, 2593 (1957).*

[2] O. A. Reutov, Proc. Acad. Sci. USSR, 87, 73 (1952); A. N. Nesmeyanov, O. A. Reutov, P. G. Knol, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 410* O. A. Reutov, Proc. Acad. Sci. USSR, 87, 991 (1952).

Received July 27, 1956

*Original Russian pagination. See C. B. Translation.

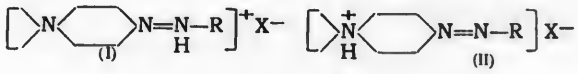
TAUTOMERISM OF SALTS OF AMINOAZO COMPOUNDS

I. N. Zhmurova

As is known, the change in color of aminoazo compounds in going from neutral or alkali to acid solutions is due to the formation of salts of the azo group: $[R-N=\underset{H}{N}-R']^+ X^-$.

The salt formation is accompanied by a displacement of the absorption band of the azo compound toward longer wavelengths: neutral solutions of the simplest azo compounds are yellow or orange, their salt solutions are red or red-violet.

With acid aminoazo compounds may give two tautomeric salts (I) and (II).

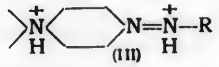


(I) (II)

A deepening of the color of aminoazo compound solutions when acidified is due to the formation of salt (I). Formation of salt (II) causes complete extinction of auxochrome. Salts of type (II) have a very weak color in the acid solution and absorb light similarly to the corresponding azobenzene derivatives not containing an amino group.

The tautomerism of salts of aminoazo compounds was first investigated by Hantzsch [1] who established that solutions of these salts were an equilibrium mixture of the tautomers (I) and (II). Their spectra consisted of two bands – in the visible [tautomer (I)] and ultraviolet regions [tautomer (II)]. The presence of two bands, corresponding to the two tautomeric salts, in the spectra of acid solutions of aminoazo compounds, was also confirmed by Badger's investigations [2].

The existence of salts of the azo group of type (I) was denied, however, by Klotz et al. [3] who considered that aminoazo compounds form salts, first of all, at the amino group of type (II). The proton was added to the azo group to form the disalt (III) only in very acid solutions.

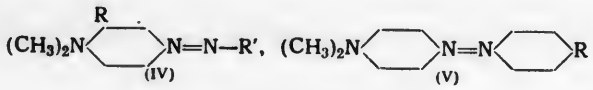


(III)

The authors drew these unexpected conclusions from data on the basicity of some azobenzene derivatives. On the basis of arithmetical calculations without taking into account the electronic reaction of groups, the authors stated that the electron density on a nitrogen atom of the azo group, in aminoazo compounds, differed little from the electron density on a nitrogen atom of an azobenzene. The electron density on a nitrogen atom of an amino group is much greater, and therefore salt formation first occurs at the amino group. Actually, in aminoazo compounds the electron density on a nitrogen atom of the azo group is considerably greater than that in an azobenzene due to the electron donor character of the amino group. Klotz's statement on the structure of salts of aminoazo compounds is, without doubt, incorrect.

It seemed interesting to study the relation between the structure of an aminoazo compound and the state of equilibrium of the tautomeric mixture. Up to now there has not been enough data available for establishing such a rule. Hantzsch [1] limited his investigations mainly to qualitative observations and did not carry out a systematic study of the salts' absorption spectra. Badger's measurements [2] covered only the simplest azobenzenes.

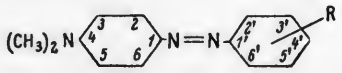
According to present-day electronic concepts, the state of equilibrium of the tautomeric mixture must depend on the distribution of electron density in the molecule of the aminoazo compound, which in its turn depends on the electronic nature and steric configuration of the substituents in the molecule. A. I. Kiprianov and I. N. Zhmurova [4] studied the effect on the state of equilibrium of a tautomeric mixture of a breakdown in coplanarity of the dimethylamino group with the benzene ring in compounds with the general formula (IV), where R – alkyl and R' – a substituted phenyl radical.



(IV) (V)

The breakdown in coplanarity of the dimethylamino group with the benzene ring hinders the transfer of electrons to the benzene ring and then to the conjugation chain of the dye. This results in a decrease in the electron density on the azo group nitrogen and an increase in electron density on the nitrogen atom of the dimethylamino group; therefore this type of dye is decolorized by acid, i.e., it mainly forms salts at the dimethylamino group of type (II). The concentration of salt (I) in the solution is very small.

The magnitude of the electron density of the azo group nitrogen atom is also affected by the substituents on the phenyl radical R'. Rogers and Campbell [5] and V. I. Kuznetsov and G. H. Kosheleva [6] measured the ionization constants of monosalts of dyes with the general formula (V) and established that electropositive substituents [R = CH_3, $C(CH_3)_3$, OCH_3] increased the ionization constants of monosalts and electronegative substituents [R = NO_2, CN, SCN, Cl, Br, I] decreased them. Sawicki, Ray and Gerber [7, 8] measured the ionization constants of aminoazobenzenes with the general formula (VI)



(VI)

The ionization constants of some compounds with the general formula (VI) are given in Table 1.

TABLE 1

No. of dye	Substituent	Position of substituent	Ionization constant (in 50% alcohol)
1	H	—	2.28
2	CH_3	2'	2.04
3	CH_3	3'	2.33
4	CH_3	4'	2.36
5	C_2H_5	2'	1.85
6	C_2H_5	4'	2.30

Methyl and an ethyl groups in positions 3' and 4' (Table 1, dyes 3, 4, 6) somewhat increase the dye's P_{Ka} due to their electron donor character. The effect of these substituents in position 2' is exactly the opposite: 4-dimethylamino-2'-methylazobenzene (Table 1, dye 2) and 4-dimethylamino-2'-ethylazobenzene (Table 1, dye 5) are weaker bases than their 4'-isomers and even weaker than dimethylaminoazobenzene. The low basicity of dyes 2 and 5 is due to the steric effect of the substituent in position 2'. Bulky substituents in a position ortho to the azo group shield the space near the azo group nitrogen atom and hinder the approach of a proton to it. The existence of shielding may be seen in the figure which represents a diagram of a 2-methylazobenzene salt molecule.

One would expect that 2'-substituted azobenzenes, in contrast to isomeric compounds, would form mainly salts of type (II). In order to check this hypothesis, we synthesized a series of known and new azo dyes with the general formula (VII)

(VII)

and measured their absorption spectra in neutral and acid alcohol solutions. The results of the measurements are given in Table 2. In acid solutions, the measurements were carried out in a mixture of concentrated hydrochloric

TABLE 2

No. of dye	Nature of R in compound (VII)	Absorption spectra in alcohol		Absorption spectra in alcoholic HCl		Melting point	Yield (in %)	Empirical formula	Results of nitrogen analysis (in %)	
		$\lambda_{max.}$ (in mμ)	$\varepsilon_{max.} \cdot 10^{-4}$	$\lambda_{max.}$ (in mμ)	$\varepsilon_{max.} \cdot 10^{-4}$				found	calculated
1	C_6H_5	420	2.80	510	4.16 [9]	117—118° [7]	60	—	—	—
2	o-$CH_3C_6H_4$	420	2.80	500	1.00 [9]	73— 74 [7]	24	—	—	—
3	p-$CH_3C_6H_4$	420	3.00	510	3.60 [9]	169—171 [7]	50	—	—	—
4	o-$C_2H_5C_6H_4$	411	2.90	500	0.44	82— 83 [7], 74— 76	3.2	$C_{16}H_{19}N_3$	16.74, 16.55	16.60
5	p-$C_2H_5C_6H_4$	415	3.07	531	4.30	131—132 [7], 136—137	77	—	—	—
6	o-$NO_2C_6H_4$	440	2.68	500	1.11 [4]	127—128 [8]	50	—	—	—
7	p-$NO_2C_6H_4$	475	3.20	508	5.68 [4]	230—231 [8]	71	—	—	—
8	2-NO_2,6-$CH_3C_6H_3$	420	1.86	480	0.40	127—129	51	$C_{15}H_{16}O_2N_4$	19.62, 19.87	19.72
9	2-CH_3,4-$NO_2C_6H_3$	476	2.64	516	1.98	161—163	68	$C_{15}H_{16}O_2N_4$	19.67, 19.54	19.72
10	2,4-$(NO_2)_2C_6H_3$ *	520	4.65	502	6.08	199—201	46	$C_{14}H_{12}O_4N_5$	22.04, 22.36	22.22
11	3,5-$(NO_2)_2C_6H_3$	481	2.16	494	4.33	215—217	90	$C_{14}H_{12}O_4N_5$	22.37, 22.23	22.22
12	o-ClC_6H_4	427	2.82	510	0.74	108—109 [8]	44	—	—	—
13	p-ClC_6H_4	420	3.03	520	3.75	158—159 [8]	40	—	—	—
14	2,4-$Cl_2C_6H_3$	435	3.16	510	0.66	142—144	44	$C_{14}H_{13}N_3Cl_2$	14.18, 14.21	14.29
15	3,5-$Cl_2C_6H_3$	440	3.08	505	4.41	115—117	40	$C_{14}H_{13}N_3Cl_2$	14.40, 14.45	14.29
16	2,4,6-$Cl_3C_6H_2$ **	405	2.52	460—470	0.45	139—140	50	$C_{14}H_{13}N_3Cl_3$	12.76, 12.92	12.79
17	o-BrC_6H_4	420	3.40	525	0.58	102—104	61	$C_{14}H_{14}N_3Br$	14.18, 14.36	13.81
18	p-BrC_6H_4	420	3.19	520	3.70	156 [10]	44	—	—	—
19	2,4-$Br_2C_6H_3$	435	3.22	507	0.67	148—150	52	$C_{14}H_{13}N_3Br_2$	Br 41.47, 41.27	Br 41.74
20	2,4,6-$Br_3C_6H_2$	405	2.38	467	0.36	160—161 [8]	62	—	—	—

* The dye is described in the patents [11] with no indication of melting point.

** The dye is described in [12] with no indication of melting point.

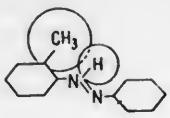


Diagram of a 2-methylazobenzene salt molecule.

acid and alcohol (1 : 2 by volume). Table 1 also gives the yields, melting points and (for the new preparations) analysis results for dyes with the general formula (VII). Actually, the effect of the substituent in position 2' differs sharply from the effect of the same substituent in position 4'. Thus, 4'-substituted dyes (3,5, 13, 18) form intensely colored red-violet salts of type (I), while their 2'-isomers (dyes 2, 4, 12, 17) are decolorized to a considerable degree by acid, i.e., form mainly salts of type (II). Such a difference in the effect of substituents in positions 2' and 4' is explained, undoubtedly, by a steric factor: in position 4' the substituents have an effect only due to their electronic nature, in position 2', it is also due to their volume. The steric dominates the electronic effect: the electronegative substituents, chlorine and bromine, (dyes 12 and 17) and the electropositive ones, methyl and ethyl, (dyes 2 and 4) promote salt formation at the dimethylamino group. The steric effect of methyl on the salt formation of 4-dimethylamino-2'-methylazobenzene was noted earlier [9]. The degree of a substituent's effect is in proportion to its volume: the methyl group decreases the absorption intensity of a salt approximately by a factor of 3.5, the larger ethyl group – by a factor of 10. Chlorine and bromine atoms, that are similar in volume to methyl, have a somewhat greater effect than methyl. Apparently, the electronic and steric effects are added together here.

4-Dimethylamino-4'-nitro- and 4-dimethylamino-2'-nitroazobenzenes (dyes 6 and 7) form salts at the azo group. The introduction of an electropositive methyl in a position ortho to the azo group decreases to a considerable degree the intensity of the absorption of the 4'-nitro derivative (dye 9) and decreases very greatly that of the 2'-nitro derivative (dye 8). The absorption maximum of the salt (480 mμ for dye 8 and 500 mμ for dye 6) is also displaced into the shorter wavelength region. The considerable displacement (20 mμ) of the absorption maximum of dye 8 as compared with that of dye 6 in a neutral medium should also be noted. Dye 8 has the same absorption maximum (420 mμ) as dye 1, which does not contain a nitro group.

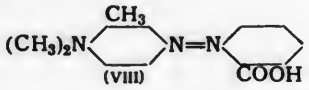
TABLE 3

No. of dye	R	Alkali solution		Acid solution	
		λ_{max} (in mμ)	$\varepsilon_{max} \cdot 10^{-4}$	λ_{max} (in mμ)	$\varepsilon_{max} \cdot 10^{-4}$
21	$C_6H_4SO_3H$	460	2.46	505	4.43 [4]
22	$2\text{-}CH_3\text{-}4\text{-}SO_3HC_6H_3$	480	1.95	510	0.50

2',4'-Disubstituted and 2',4',6'-trisubstituted dyes (14, 16, 19, 20) also form salts mainly at the dimethylamino group. The absorption band of trisubstituted dye salts is strongly displaced toward shorter wavelengths.

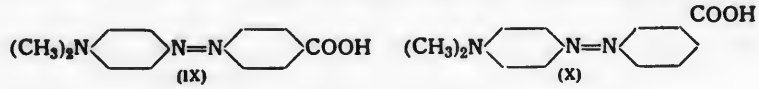
We also investigated the effect of substituents in a position ortho to the azo group on the properties of indicator dyes – methyl orange and methyl red and its isomers. Table 3 gives the absorption maxima and molecular extinctions in alkali and acid media of methyl orange and its methyl homolog.

In this case the effect of the methyl is very great. The absorption intensity of dye 22 in an acid medium is almost a factor of 9 less than that of dye 21. Dye 22 was decolorized by acid and was of no use as an indicator. The deterioration in indicator properties of dyes of the methyl orange type due to steric hindrances on introducing substituents (halides) into one or two positions ortho to the azo group was noted earlier [5].



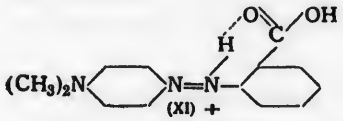
(VIII)

As has been shown [4], the methyl homolog of methyl red (VIII) has optical and indicator properties practically identical with those of methyl red, i.e., the existence of steric hindrances in the molecules has no effect on the dye's properties. In isomeric meta- and para-methyl reds (IX) and (X), methyl has its usual effect:



(IX) (X)

The methyl homologs of meta- and para-methyl red are to a considerable degree decolorized by acid. The unusual properties of methyl red and its methyl homolog are due, according to the authors, to the presence of a hydrogen bond in the molecule of the dye's salt (XI).

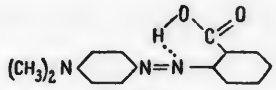


(XI)

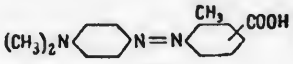
At the present time a ring structure, due to the presence of a hydrogen bond between the hydrogen atom of the carboxyl group and the nitrogen atom of the azo group, is accepted for methyl red even in a neutral medium (XIII) [13].

It seemed interesting to find out whether the ortho-isomer would differ from the meta- and para-isomers of dyes with the general formula (XIII).

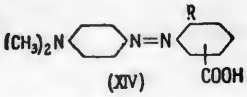
Table 4 gives optical data for methyl red, its isomers and their methyl homologs with the general formula (XIV).



(XII)



(XIII)



(XIV)

The absorption intensity of the ortho-methyl homolog of methyl red is a factor of 2.4 less than that of methyl red itself. The ortho-methyl has a strong effect but not as strong as in the isomeric dyes. It should be noted that both the positions ortho to the azo group are substituted in dye 24 and due to this the access to the nitrogen atom of the azo group is more difficult for a proton than in dyes 26 and 28. In spite of this, the effect

TABLE 4

No. of dye	R	COOH position	Alkali solution		Acid solution	
			λmax (in mμ)	$\varepsilon_{max} \cdot 10^{-4}$	λmax (in mμ)	$\varepsilon_{max} \cdot 10^{-4}$
23	H	ortho-	435	1.90	520	4.54 [4]
24	CH_3	ortho	415	1.60	515	1.88
25	H	para-	455	2.65	515	6.00 [4]
26	CH_3	para-	446	2.42	510	1.20
27	H	meta-	435	2.35	513	4.10 [4]
28	CH_3	meta	440	2.30	506	1.00

of methyl is less in dye 24 than in dyes 26 and 28. In all probability, the reason for this is the existence of a hydrogen bond between the nitrogen atom of the azo group and the carboxyl.

EXPERIMENTAL

The azo dyes were prepared by the usual method: appropriate aniline derivatives were dissolved in hydrochloric acid, diazotized and coupled with dimethylaniline, dissolved in dilute hydrochloric acid. After some time the calculated amount of sodium acetate was added. The precipitated dye was filtered off and purified by recrystallization. In this way we prepared dyes 1-9, 11-20, 24, 26, and 28. The yields (for the crude materials), melting points and analysis results of dyes 1-20 are given in Table 2, for dyes 24, 26 and 28 they are given below. Dyes 4, 5, 8, 10, 14, 15, 17, 19 were recrystallized from alcohol, 9 – from ligroin, 11 – from benzene, 16 – from glacial acetic acid and 24, 26 and 28 – from toluene.

4-Dimethylamino-2'-methyl-6'-carboxyazobenzene (24). The yield was 11%. The m. p. was 152-153°.

Found %: N 14.66, 14.48. $C_{16}H_{17}O_2N_3$. Calculated %: N 14.84.

4-Dimethylamino-2'-methyl-4'-carboxyazobenzene (26). The yield was 90%. The m. p. was 218-219°.

Found %: N 15.15, 14.84. $C_{16}H_{17}O_2N_3$. Calculated %: N 14.84.

4-Dimethylamino-2'-methyl-5'-carboxyazobenzene (28). The yield was 67%. The m. p. was 203-205°.

Found %: N 14.81, 14.66. $C_{16}H_{17}O_2N_3$. Calculated %: N 14.84.

4-Dimethylamino-2',4'-dinitroazobenzene. 5 g of dinitroaniline was dissolved in 25 ml of concentrated sulfuric acid at 0° and 2 g of solid sodium nitrite added. The mixture was stirred for 30 minutes at 60° and poured onto ice. A solution of 5 g of dimethylaniline in dilute hydrochloric acid was added. After some time soda was added. The precipitated dye was filtered off and purified by recrystallization from nitrobenzene and then from alcohol. The yield of the crude preparation was 4 g.

4-Dimethylamino-2'-methyl-4'-sulfoazobenzene (22). 1 g of 2-methylsulfanilic acid and 0.6 g of dimethylaniline were mixed with 10 ml of water. The mixture was cooled and a solution of 0.4 g of sodium nitrite in 10 ml of water was added dropwise. Stirring was continued for 10 minutes. By adding sodium chloride, we precipitated 1.2 g of the sodium salt of the dye. The salt was dissolved in water by heating, and after cooling the solution, acetic acid was added dropwise. After half an hour crystals of the free sulfoacid precipitated and these were filtered off and recrystallized from water. The yield was 60%.

Found %: N 10.88, 11.18. $C_{15}H_{17}O_3N_3S \cdot 3H_2O$. Calculated %: N 11.08. (Water of crystallization was proved to be present).

SUMMARY

1. We measured the absorption spectra of 24 aminoazo dyes, including 13 new ones, in neutral and acid media.

2. It was shown that aminoazo dyes containing substituents in position 2' form salts mainly at the dimethylamino group.

LITERATURE CITED

[1] A. Hantzsch, F. Hilscher, Ber. 41, 1171 (1908); A. Hantzsch, Ber. 42, 2129 (1909); 46, 1537 (1913); 48, 167 (1915); A Hantzsch, W. Voigt, Ber. 62, 973 (1929); A. Hantzsch, A. Burawoj, Ber. 63, 1760 (1930).

[2] G. M. Badger, R. G. Buttery, C. E. Levis, J. Chem. Soc. 1954, 1888.

[3] J. M. Klotz, H. A. Fiess, J. Y. Chen Ho, M. Mellody, J. Am. Chem. Soc. 75, 5135 (1954).

[4] A. I. Kiprianov and I. N. Zhmurova, J. Gen. Chem. 23, 626 (1953).*

[5] M. Rogers, T. Campbell, J. Am. Chem. Soc. 73, 5122 (1951).

[6] V. I. Kuznetsov and G. N. Koseheleva, J. Anal. Chem. 7, 57 (1952)*.

[7] E. Sawicki, F. Ray, J. Org. Ch. 19, 1686 (1954).

[8] E. Sawicki, D. Gerber, J. Org. Ch. 21, 4101 (1956).

[9] J. A. Miller, R. W. Sapp, E. C. Miller, J. Am. Chem. Soc. 70, 3458 (1948).

[10] H. Holdschmidt, B. Bardach, Ber. 25, 1374 (1892).

[11] Brit. Pat. 263479; Zbl. 1927, I, 2359; Brit. Pat. 244143; Zb. 1926, I, 2970.

[12] J. A. Miller, R. W. Sapp, E. C. Miller, Cancer Research 9, 652 (1949); Ch. A. 1950, 3132.

[13] W. Ross, G. Warwick, Chem. Ind. 1955, 745.

Received July 11, 1956

Institute of Organic
Chemistry of the Academy of Sciences
Ukr. SSR

* Original Russian pagination. See C. B. Translation.

REACTION OF HALOGEN EXCHANGE IN α-CHLORO SULFIDES

K. A. Petrov and G. A. Sokolsky

Up to now practically nothing is known about the mono-α-fluoro sulfides. In the paper by Bohme the statement was made that "the treatment of α-halo sulfides with anhydrous liquid hydrogen fluoride in copper or platinum apparatus results in halogen-exchange and the formation of α-fluoro sulfides" [1]. The preparation of fluoromethyl methyl sulfide and fluoromethyl ethyl sulfide was mentioned in this paper; however, data on the physical and chemical properties of the indicated sulfides is completely absent. * The present study is devoted to seeking a method for the replacement of the chlorine atoms in α-chloro sulfides by fluorine.

Originally we proposed to exchange the halogens in α-chloro sulfides by means of metal fluorides; however, it was found that bis(chloromethyl) sulfide does not react with potassium fluoride even at 170°. The heating of the sulfide with antimony fluoride at 130-140° gave tarry products, from which we were unable to isolate any individual substances. When the reaction was run at a lower temperature, the starting sulfide was recovered unchanged. A similar result was obtained when the bis(chloromethyl) sulfide was heated with mercury fluoride, zinc fluoride, or potassium bifluoride.

We were able to effect the replacement of the chlorine atoms in α-chloro sulfides by fluorine only by using anhydrous hydrogen fluoride. This reaction was studied on the examples of reacting benzyl chloromethyl sulfide, β-chloroethyl chloromethyl sulfide, ethyl chloromethyl sulfide and bis(chloromethyl) sulfide with liquid hydrogen fluoride. Here it was established that the halogen exchange, accompanied by the evolution of hydrogen chloride, proceeds even at room and lower temperatures, and only if a large excess of anhydrous liquid hydrogen fluoride is used. Thus, the quantitative amount of hydrogen chloride was evolved when a mixture of benzyl chloromethyl sulfide and a 3-fold excess of hydrogen fluoride was kept at room temperature for 2-2.5 days. Removal of the excess hydrogen fluoride left a viscous yellow substance, which attacked glass and began to decompose even at 50-60°. Fractionation of the substance in a high vacuum gave benzyl fluoromethyl sulfide; the found values of the molecular weight and amounts of carbon, hydrogen, fluorine and sulfur agreed with the calculated. The structure of the benzyl fluoromethyl sulfide was proved by its conversion into benzyl methoxymethyl sulfide; the latter proved to be identical with the reaction product of sodium benzylmercaptide and chloromethyl methyl ether. Without doubt, the reaction of hydrogen fluoride with benzyl chloromethyl sulfide results in halogen exchange, and benzyl fluoromethyl sulfide is formed:

$$C_6H_5CH_2—S—CH_2Cl + HF \rightarrow C_6H_5CH_2—S—CH_2F + HCl.$$

In a similar manner β-chloroethyl chloromethyl sulfide gave β-chloroethyl fluoromethyl sulfide.

A quantitative evolution of hydrogen chloride was also observed in the reaction of ethyl chloromethyl sulfide with anhydrous liquid hydrogen fluoride; however, instead of ethyl fluoromethyl sulfide we unexpectedly obtained a different substance here, which in its physical properties and elementary composition corresponded to propylene thiooxide. The structure of this last compound was proved by its conversion into the β-chloro-n-propyl ester of thiolchloroacetic acid when reacted with chloroacetyl chloride:

$$CH_3—CH—CH_2 \quad (S) + ClCH_2—CO—Cl \rightarrow ClCH_2CO—SCH_2CHClCH_3.$$

* In the paper it was stated that the dissertation of Fuisting (Berlin, 1939), devoted to the problems of the synthesis of α-fluoro ethers and α-fluoro sulfides, was destroyed in connection with the war activities in 1945.

The formation of propylene thiooxide in the reaction of ethyl chloromethyl sulfide with anhydrous hydrogen fluoride can be explained only by the decomposition of the intermediately formed unstable ethyl fluoromethyl sulfide

$$CH_3CH_2{-}S{-}CH_2Cl + HF \rightarrow CH_3CH_2{-}S{-}CH_2F + HCl$$

$$CH_3CH_2{-}S{-}CH_2F \rightarrow CH_3\underset{\diagdown S \diagup}{CH{-}CH_2} + HF$$

As a result, also in the reaction of ethyl chloromethyl sulfide with hydrogen fluoride there occurs halogen exchange and the formation of the α-fluoro sulfide, which suffers further transformation.

Great difficulties arose in the preparation of the bis(fluoromethyl) sulfide. Characteristic for the vast majority of the experiments run in connection with studying the reaction of bis(chloromethyl) sulfide with hydrogen fluoride was the evolution of hydrogen chloride and the formation of a solid polymer. We were able to isolate a low-boiling reaction product only in the case where the reaction of the bis(chloromethyl) sulfide with a 2.5-fold amount of anhydrous hydrogen fluoride was run with cooling to −10° for 6-8 hours. The fluoroorganic product was isolated by fractionation of the reaction mixture in vacuo at low temperature. The substance obtained here strongly attacks glass, fumes in the air, decomposes in the presence of potassium fluoride, and even when kept at 0°, it polymerizes with the evolution of hydrogen fluoride. The isolated low-boiling substance did not contain chlorine, and based on the amount of carbon, hydrogen, fluorine and sulfur, and also from the molecular weight, the substance corresponded to bis(fluoromethyl) sulfide. The conversion of this compound into the symmetrical bis(methoxymethyl) sulfide can serve as proof of its structure. The latter proved to be identical with the substance obtained by the reaction of bis(chloromethyl) sulfide with sodium methylate. Consequently, in the reaction of bis(chloromethyl) sulfide with hydrogen fluoride the bis(fluoromethyl) sulfide is formed as the result of halogen exchange: $S(CH_2Cl)_2 + 2HF \rightarrow S(CH_2F)_2 + 2HCl$. However, the bis(fluoromethyl) sulfide is an unstable compound and exists mainly only at low temperature. This is the probable reason for the failure of the attempts to obtain it by the treatment of the chloro sulfide with metal fluorides, and also for the absence of any data in the literature on bis(fluoromethyl) sulfide.

EXPERIMENTAL

Benzyl Fluoromethyl Sulfide (I). Nine grams of benzyl chloromethyl sulfide and 11 g of anhydrous hydrogen fluoride was mixed in a copper test tube at −10°, and the mixture was gradually warmed to room temperature. Here the evolution of hydrogen chloride was observed, which ceased after two days. Then the mixture was treated with 150 ml of dry ether, and after cooling to −15° the addition of 40 g of powdered anhydrous potassium fluoride was made in portions and with stirring. The precipitate was filtered, and the filtrate was evaporated in vacuo at room temperature. The residue (5.7 g) was a viscous yellow liquid that attacked glass. Fractionation gave 4.1 g of a colorless viscous liquid with b. p. 25-28° (0.1 mm), which proved to be (I).

Found %: C 61.93; H 5.89; F 12.9; S 20.20; Cl absent. M 158.5. C_8H_9FS. Calculated %: C 61.54; H 5.77; F 12.2; S 20.51. M 156.2.

When heated to 50-60° (I) decomposes with the evolution of hydrogen fluoride and the formation of tarry substances. Water rapidly hydrolyzes the compound with the evolution of hydrogen fluoride and the formation of an amorphous precipitate. The compound is readily soluble in alcohol, ether, benzene and carbon disulfide. The evolution of hydrogen fluoride is observed when its alcohol solutions are heated.

Benzyl Methoxymethyl Sulfide (II). A. To a solution of 5.2 g of (I) in 20 ml of methanol, with ice-cooling and stirring, was slowly added in drops a solution of 0.7 g of metallic sodium in 10 ml of methanol. The formation of a finely crystalline precipitate was observed here. The mixture was warmed to room temperature and stirred for 1 hour. Then 20 ml of alcohol was distilled from the mixture, and the residue was diluted with 30 ml of water and then extracted 3 times with ether. The ether extracts were dried over calcium chloride. The solution was evaporated, and the residue was fractionated twice in vacuo. We isolated 4.5 g (80%) of (II) with b. p. 114.5-115° (12 mm), d_4^{20} 1.0741, n_D^{20} 1.5548.

Found %: C 64.46; H 7.01; S 18.89. $C_9H_{12}OS$. Calculated %: C 64.72; H 7.19; S 19.06.

B. A solution of 2.3 g of metallic sodium in 50 ml of methanol was treated with 12.4 g of benzyl mercaptan, and then 8.9 g of chloromethyl methyl ether was added slowly in drops. The deposition of a crystalline precipitate was observed. Then the mixture was treated in the same manner as in A. We isolated 12.6 g (75%) of (II) with b. p. 115° (12 mm), d_4^{20} 1.0745, n_D^{20} 1.5546.

β-Chloroethyl Fluoromethyl Sulfide (III). A mixture of 8 g of β-chloroethyl chloromethyl sulfide and 8.5 g of anhydrous hydrogen fluoride, under the same conditions as in the preparation of (I), gave 5.9 g of viscous light-yellow liquid with b. p. 31-32° (1 mm), which proved to be (III).

Found %: F 14.1; Cl 27.91; S 24.58. M 130.6. C_3H_6ClFS. Calculated %: F 14.8; Cl 27.63; S 24.90. M 128.5.

(III) attacks glass; when kept for 5 or more days, and also when heated to 50-60°, it decomposes with the evolution of hydrogen fluoride and the formation of tarry substances.

Reaction of Ethyl Chloromethyl Sulfide With Hydrogen Fluoride. Ten grams of ethyl chloromethyl sulfide and 10 g of anhydrous hydrogen fluoride were mixed in a copper test tube at −10°. The mixture was kept at room temperature for 2 days, diluted with 100 ml of ethyl chloride, and then the mixture was treated with 40 g of powdered potassium fluoride, added in small portions at −15°. The precipitate was filtered, the mother liquor was evaporated, and the residue was fractionated. We isolated 2.9 g of starting ethyl chloromethyl sulfide and 4.4 g of propylene thiooxide with b. p. 77-79°, d_4^{20} 0.9588, n_D^{20} 1.4685 (the literature for propylene α-thiioxide gives b. p. 75-78°, d_4^{19} 0.964, n_D^{19} 1.473).

Found %: C 48.41; H 7.42. M 75.5. C_3H_6S. Calculated %: C 48.65; H 7.77. M 74.1.

A mixture of 2.5 g of propylene thiooxide and 3.8 g of chloroacetyl chloride was heated for 30 minutes on the water bath and then fractionated. We obtained 4.1 g (65%) of the β-chloro-n-propyl ester of thiolchloroacetic acid with b. p. 90-90.5° (4 mm), d_4^{18} 1.3162, n_D^{18} 1.5190 (the literature for β-chloro-n-propyl thiolchloroacetate gives b. p. 85° (2 mm), d_4^{18} 1.3125, n_D^{18} 1.5201).

Found %: C 32.48; H 4.58; Cl 37.29; S 17.04. $C_5H_8OCl_2S$. Calculated %: C 32.10; H 4.31; Cl 37.90; S 17.14.

Bis(fluoromethyl) Sulfide (IV). Thirty grams of bis(chloromethyl) sulfide and 26 g of anhydrous hydrogen fluoride were mixed in a copper test tube at −10°. The mixture was kept at this temperature for 6-8 hours, and here 10.1 g of hydrogen chloride was evolved. The reaction products were vacuum-distilled at 5 mm and a temperature of −10°, with condensation of the distillate in a copper trap, cooled with a mixture of acetone and solid carbon dioxide; we obtained 27 g of a liquid condensate. The residue consisted of 9 g of tarry substance and 5 g of the starting chloro sulfide. Subsequent 2-fold fractionation of the condensate in a vacuum of 60-80 mm and a temperature of −10° resulted in the evolution of hydrogen fluoride, while the vacuum-distillation at 5 mm gave 7.1 g of colorless liquid which strongly attacked glass, fumed in the air, and proved to be (IV) with b. p. from −25 to −22° (3 mm).

Found %: C 24.01; H 3.66; F 37.99; S 32.11; Cl absent. M 101.6. $C_2H_4F_2S$. Calculated %: C 24.49; H 4.08; F 38.78; S 32.65. M 98.1.

(IV) decomposes at room temperature with the evolution of hydrogen fluoride and the formation of a greyish amorphous powder, insoluble in water and in organic solvents.

Bis(methoxymethyl) Sulfide (V). A. From 3.1 g of (IV) and a solution of 1.5 g of metallic sodium in 10 ml of methanol, under the same conditions as in the preparation of (II), we obtained 2.4 g (60%) of (V) with b. p. 152-153.5° (755 mm) or 50-52° (15 mm), d_4^{20} 1.0514, n_D^{20} 1.4541 (the literature for bis(methoxymethyl) sulfide gives b. p. 152-154° from 740 mm).

Found %: S 26.12. $C_4H_{10}O_2S$. Calculated %: S 26.23.

B. From 12.2 g of bis(chloromethyl) sulfide and a solution of 5.4 g of metallic sodium in 100 ml of methanol, under the same conditions as in the preparation of (II), we obtained 9.0 g (83%) of (V) with b. p. 152-153°, d_4^{20} 1.0502, n_D^{20} 1.4532.

SUMMARY

A number of α-fluoro sulfides were prepared by the replacement of the chlorine atoms in α-chloro sulfides by fluorine. It was established that the α-fluoro sulfides are unstable compounds, decomposing under ordinary conditions with the evolution of hydrogen fluoride.

LITERATURE CITED

[1] H. Böhme, H. Fischer, R. Frank, Lieb. Ann. 563, 54 (1949).

Received July 3, 1957

REACTION OF ORGANOSILICON COMPOUNDS WITH PHOSPHORUS CHLORIDES

A. P. Kreshkov and D. A. Karateev

Up to now the reaction of organosilicon compounds with phosphorus halides has received comparatively little study. The reaction of phosphorus pentachloride with tetraethoxysilane was first studied by D. I. Mendeleev in 1860 [1]. A different reaction course in the reactions of tetraethoxysilane and tetraphenoxysilane with phosphorus oxychloride was indicated by Stokes [2, 3]. The reactions were run by him with heating of the reactant mixtures in sealed tubes. This technique gave $SiP_2O_6Cl_2$, and also $PO(OC_6H_5)Cl_2$, $PO(OC_6H_5)_2$ and $PO(OC_6H_5)_3$. The products of the reaction of organosilicon compounds with inorganic and also with organic compounds of phosphorus have been studied by a number of investigators [4-9].

Organo-silicon-phosphorus compounds have begun to assume industrial importance in recent years [10, 11].

As the result of our studies, it was established that the boiling of a mixture of the proper tetraalkoxysilane with phosphorus oxychloride yields solid polymeric organo-silicon-phosphorus compounds, corresponding to the following formulas: $Si_4P_3C_3H_{13}O_{19}$, $Si_2P_2C_2H_{10}O_{12}$ and $Si_3P_2C_4H_{16}O_{15}$.

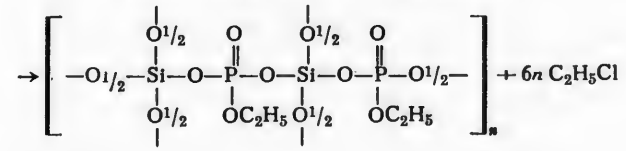
It was postulated that the reaction between tetraalkoxysilanes and phosphorus oxychloride proceeds in a stepwise manner. For example, the reaction between $Si(OC_2H_5)_4$ and $POCl_3$ proceeds in accordance with the following equations:

$$3Si(OC_2H_5)_4 + 4POCl_3 \rightarrow 3SiCl_4 + 4PO(OC_2H_5)_3,$$

$$2PO(OC_2H_5)_3 + POCl_3 \rightarrow 3PO(OC_2H_5)_2Cl,$$

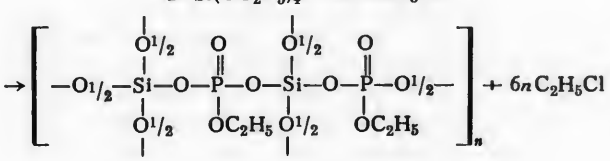
$$SiCl_4 + Si(OC_2H_5)_4 \rightarrow 2Si(OC_2H_5)_2Cl_2,$$

$$2n\ Si(OC_2H_5)_2Cl_2 + 2n\ PO(OC_2H_5)_2Cl \rightarrow$$



The total reaction can be depicted by the scheme

$$2n\ Si(OC_2H_5)_4 + 2n\ POCl_3 \rightarrow$$



The obtained product suffers partial hydrolysis. The hydrolysis is accompanied by replacement of some of the OC_2H_5 groups by OH groups and the addition of a molecule of water. The substance formed here has the composition $Si_2P_2C_2H_{10}O_{12}$.

Proof that the reaction proceeds in accordance with the above given total scheme is the fact that in each of the investigated reactions between $Si(OR)_4$ (where R = CH_3, C_2H_5 or n-C_4H_9) and $POCl_3$ the corresponding alkyl chloride is liberated and organo-silicon-phosphorus compounds of the indicated composition and structure are formed. In addition, in some cases small amounts of intermediate reaction products were isolated (alkoxychlorosilanes and mixtures of organic phosphorus compounds with organosilicon products). It was also shown that under different reaction conditions these products cannot be isolated. After purification the obtained organo-silicon-phosphorus compounds were analyzed. Their structure was established by chemical, physicochemical and physical (infrared spectroscopy) methods of analysis. It was also established by us that transesterification takes place when a mixture of a tetraaroxysilane with either PCl_3 or $POCl_3$ is boiled in anhydrous benzene solution.

$$3Si(OC_6H_5)_4 + 4PCl_3 \rightarrow 3SiCl_4 + 4P(OC_6H_5)_3$$
$$3Si(OC_6H_4CH_3)_4 + 4POCl_3 \rightarrow 3SiCl_4 + 4PO(OC_6H_4CH_3)_3$$

Triphenyl phosphite and tri-o-cresyl phosphate were isolated when the mixtures were distilled.

EXPERIMENTAL

The starting substances were phosphorus oxychloride and phosphorus trichloride, and also the esters of orthosilicic acid, synthesized by us using the methods described in the literature [12, 13]. The physical constants of the starting substances are given in Table 1.

TABLE 1

Physical Constants of Starting Substances

Formula of substance	Boiling point	n_D^{20}	d_4^{19}
$Si(OCH_3)_4$	121—122°	1.3694	1.025
$Si(OC_2H_5)_4$	166—167	1.3850	0.932
$Si(OC_4H_9)_4$	273—275 (758 мм)	1.414	0.909
$Si(OC_6H_5)_4$*	417—420	—	—
$Si(OC_6H_4CH_3)_4$	435—438	—	—
PCl_3	75—76	—	1.583
$POCl_3$	106.5—107.3	—	1.681

* B. p. 47.8°.

Reaction of Tetraalkoxysilanes With Phosphorus Oxychloride

Either 0.2 mole of tetramethoxy- or tetraethoxysilane or 0.1 mole of tetrabutoxysilane was mixed with 0.1 mole of phosphorus oxychloride in a 100 ml round-bottomed flask, connected to a reflux condenser through a ground-glass connection. The mixture was heated at boiling in an oil bath, and for the tetramethoxysilane the boiling time was 15 minutes, for tetraethoxysilane it was 3 hours, and for tetrabutoxysilane it was 4 hours. The corresponding alkyl chloride was liberated during boil. The mixture of reaction products was fractionally distilled. Removal of the volatile compounds left a solid residue, representing the organo-silicon-phosphorus compound. In addition to the main reaction product, the esters of orthosilicic acid, organic phosphorus compounds and other compounds were obtained as impurities. The obtained organo-silicon-phosphorus compounds were purified by refluxing them with cryoscopic benzene (50 ml of benzene for 2 g of substance) for 20-25 minutes, after which the precipitate was filtered, washed with alcohol and benzene, dried to constant weight at 85-90°, and ground to a powder. The purified and dried organo-silicon-phosphorus products were stored in receptacles

TABLE 2

Analysis of Reaction Products of Tetraalkoxysilanes with Phosphorus Oxychloride

Starting substances	Empirical formula of obtained compound	P(in %)		Si(in %)		C(in %)		H(in %)		OR(in %)		Groups and bonds shown by the method of IR-spectroscopy	n_D^{20}
		Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated		
$Si(OCH_3)_4 + POCl_3$	$Si_4P_3C_3H_{13}O_{19}$ (I)	16.67, 16.89	16.64	20.06, 19.88	20.12	6.31, 6.89, 6.41	6.45	2.47, 2.43, 3.08	2.35	16.18, 16.49	16.67	O—H Si—O P—O P=O P—OCH_3 C—$H(CH_3)$	2.01
$Si(OC_2H_5)_4 + POCl_3$	$Si_2P_2C_2H_{10}O_{12}$ (II)	17.73, 18.09	17.97	16.16, 16.05	16.32	7.14, 7.05	6.97	3.10, 3.06	2.93	12.79, 12.36	13.09	O—H Si—O P—O P=O P—OC_2H_5 C—$H(CH_3)$	1.68
$Si(OC_4H_9)_4 + POCl_3$	$Si_3P_2C_4H_{16}O_{15}$ (III)	13.95, 14.05	13.75	18.65, 18.50	18.71	10.93, 10.59	10.67	3.62, 3.87	3.58	—	—	O—H Si—O P=O P—O P—OC_4H_9 C—$H(CH_3)$ P—OH	1.73

placed in a desiccator over P_2O_5. The purified substances are either white or slightly yellow solids, insoluble in all of the ordinary organic solvents, but soluble with decomposition in warm dilute NaOH solution.

The organo-silicon-phosphorus compounds were analyzed for silicon, phosphorus, carbon, hydrogen and alkoxy groups, and were also investigated by the methods of infrared spectroscopy and x-ray structure analysis. Phosphorus was determined by the method of dissolving a known weight of the investigated substance in warm standard NaOH solution and back-titrating with HCl solution. Silicon was determined by the photocolorimetric method, which made it possible to analyze for silicon in the presence of phosphorus [14]. Carbon and hydrogen were determined by the microcombustion of weighed samples of the substances in the presence of Cr_2O_3 catalyst [15, 16]. The alkoxy groups were determined by the semimicro method [17]. The densities of the solid products were determined by the Lunge method. An IKS-11 spectrometer with sodium chloride prism was used to take the infrared spectra of the solid organo-silicon-phosphorus compounds. The substances were taken pressed in a potassium bromide tablet (10 mg of substance per gram of KBr).

When the infrared spectra were deciphered, the following characteristic frequencies of the atomic groupings and bonds in the investigated organo-silicon-phosphorus compounds were established.

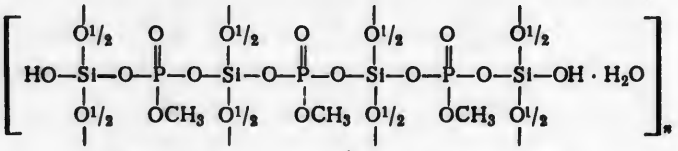
1. For $Si_4P_3C_3H_{13}O_{19}$ (I): 2.98 μ (—OH), 3.45 & 7.18 μ [C—H(CH_3)], 10.43 μ (P—O), 8.19 μ (P=O), 9.65 μ (Si—O) & 9.12 μ (P—OCH_3).
2. For $Si_2P_2C_2H_{10}O_{12}$ (II): 2.98 μ (—OH), 3.43 & 7.18 μ [C—H(CH_3)], 10.45 μ (P—O), 8.05 μ (P=O), 9.8 μ (Si—O), 9.2 μ (P—OC_2H_5).
3. For $Si_3P_2C_4H_{16}O_{15}$ (III): 2.95 μ (—OH), 3.46 & 7.16 μ [C—H(CH_3)], 10.73 μ (P—O), 8.1 μ (P=O), 9.8 μ (Si—O), 3.70 μ (P—OH) и 9.18 μ (P—OC_4H_9).

Relating the obtained absorption maxima to the proper groups and bonds was done on the basis of studies [18-21].

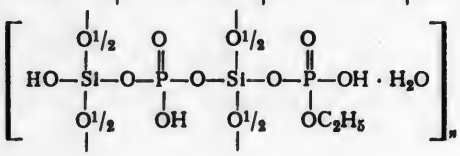
The analysis results for the obtained organo-silicon-phosphorus compounds are given in Table 2.

X-ray structure analysis revealed that the investigated products are not crystalline.

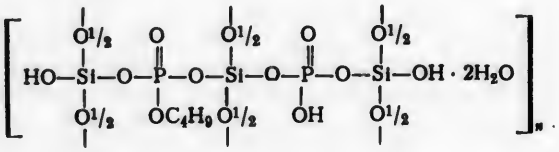
Based on the analysis results the following structural formulas were established for one (unit) link of the macromolecule of the obtained solid polymeric organo-silicon-phosphorus compounds:



(I)



(II)



(III)

The yields of the organo-silicon-phosphorus products in percent of the theoretical, based on the amount of added $POCl_3$, were respectively 75-80, 25-30 and 30-35% for compounds (I), (II) and (III). The mean values of the physical constants and the chemical analysis data are listed in Table 3.

Transesterification of Tetraaroxysilanes With Phosphorus Trichloride or With Phosphorus Oxychloride

We studied the reaction of tetraphenoxysilane with phosphorus trichloride, and also that of tetracresoxysilane with phosphorus oxychloride.

TABLE 3

Physical Constants and Chemical Analysis Data for the Reaction Products of Tetraalkoxysilanes With Phosphorus Oxychloride

Substance formula	Boiling point	d_4^{20}	n_D^{20}	Molecular weight		Si(in %)		Cl(in %)	
				found	calc.	found	calc.	found	calc.
$n\text{-}C_3H_7Cl$	46—47°	0.8916	1.3892	77.6	78.5	—	—	—	—
$n\text{-}C_4H_9Cl$	77.3—78	0.8866	1.40.8	91.3	92.5	—	—	—	—
$Si(OC_4H_9)_3Cl$	126—128 (10 мм)	0.9705	1.4175	277.0	282.8	9.45	9.91	12.45	12.53
$Si(OC_4H_9)_2Cl_2$ . . .	82—84 (7.5 мм)	1.059 (d_4^{17})	1.4208	235.5	245.2	11.72	11.44	29.30	28.93

TABLE 4

Substance formula	Boiling point at 758 mm	d_4^{20}	Molecular weight		C(in %)		H(in %)		Characteristic frequencies in the IR-spectra and the groups and bonds corresponding to them
			found	calc.	found	calc.	found	calc.	
$P(OC_6H_5)_3$	359—360°	1.181	308.2, 313.0	310.3	69.41, 69.27	69.68	4.90, 4.83	4.87	C_6H_5 (3.30 μ) P—O (10.50 μ) P—OC_6H_5 (9.70 μ) C_6H_5 (6.2 μ)
$PO(OC_6H_4CH_3\text{-}o)_3$	409—410	1.7905	361.8, 373.5	368.4	69.05, 68.39	68.47	5.11, 5.33	5.74	C_6H_5 (3.23 μ) C—H(CH_3) (3.42μ) P=O (7.69 μ) P—$OC_6H_4CH_3$-*o* (9.65 μ) P—O (10.42μ) C_6H_5 (6.19 μ)

As the result of studying the indicated reactions in the presence and in the absence of a solvent (anhydrous benzene) and a catalyst (anhydrous $AlCl_3$), it was found that the best yields of the corresponding esters of phosphorus and phosphoric acid are obtained when benzene is added to the reaction mixture. Evidently, when $AlCl_3$ is added to the reaction mixture the catalyst reacts with the intermediately formed haloesters of orthosilicic acid, leading to the formation of aluminosilicates. The silicon tetrachloride, evolved at a more rapid rate in the presence of $AlCl_3$, was trapped and identified (d_4^{20} 1.50, b. p. 56-58°).

A new method was developed by us for the preparation of triaryl phosphites and triaryl phosphates, involving the reaction of tetraaroxysilanes with phosphorus trichloride or with phosphorus oxychloride. The reaction was accomplished by preparing a mixture of 0.075 mole of tetraphenoxysilane and phosphorus trichloride, or of tetracresoxysilane and phosphorus oxychloride, and boiling the mixture in the presence of 30 ml of anhydrous benzene for 15 hours in a round-bottom flask under reflux, after which the reaction mass was distilled. Distillation in the first case gave unreacted phosphorus trichloride (77-79°), benzene, containing phosphorus trichloride (79-86°), and triphenyl phosphite (358-361°). In the second case distillation gave benzene, containing phosphorus oxychloride (81-90°), unreacted phosphorus oxychloride (104-112°) and tri-o-cresyl phosphate (405-410°). Redistillation through a Vigreaux column gave triphenyl phosphite with b. p. 359-360° (corr.) and tri-o-cresyl phosphate with b. p. 409-410° (corr.) (758 mm) in 20-30% yield.

The physical constants of the obtained products and the results of their chemical analysis are given in Table 4. The composition and structure of these compounds was confirmed by their infrared spectra.

SUMMARY

1. The reaction of tetramethoxysilane, tetraethoxysilane, tetra-n-butoxysilane and tetra-o-cresoxysilane with phosphorus oxychloride was studied, and also that of tetraphenoxysilane with phosphorus trichloride. Three new organo-silicon-phosphorus compounds were obtained by us. The structures of the obtained compounds were established by chemical, physicochemical and physical methods of analysis.

2. New methods were developed for the preparation of triphenyl phosphite and tri-o-cresyl phosphate, based on the reaction of tetraaroxysilanes with phosphorus trichloride or with phosphorus oxychloride.

3. Schemes were proposed for the reaction between tetraalkoxysilanes and phosphorus oxychloride, and also between tetraaroxysilanes and phosphorus trichloride or phosphorus oxychloride.

LITERATURE CITED

[1] D. I. Mendeleev, Gornyi Zhur. [Mining J.], No. 8, 202 (1860).

[2] H. N. Stokes, Ber. 24, 933 (1891).

[3] H. N. Stokes, Am. Chem. J. 14, 545 (1892).

[4] C. Friedel, A. Landenburg, Ber. 3, 15 (1870).

[5] B. A. Arbuzov and A. N. Pudovik, Proc. Acad. Sci. USSR 59, 1433 (1948).

[6] K. C. Frisch, H. Lyons, J. Am. Chem. Soc. 75, 4078 (1953).

[7] A. D. Petrov, A. F. Mironov and V. G. Glukhovtsev, Proc. Acad. Sci. USSR 93, 499 (1953).

[8] A. Ya. Yakubovich and G. V. Motsarev, J. Gen. Chem. 23, 1547 (1953).*

[9] M. G. Voronkov, J. Gen. Chem. 25, 469 (1955). *

[10] Brit. Patent 706,781 (1954); J. Appl. Chem. 4, 538 (1954); Abstract Journal, Chemistry, No. 3, 376, 8243 II (1956).

[11] U. S. Patent 2488449 (1949); Ch. A. 44, 2287 (1950).

[12] G. F. Yakimovich, Dissertation: "Qualitative Analysis of Organosilicon Compounds by Infrared Spectroscopy," D. I. Mendeleev Chem.-Tech. Inst., Moscow (1952).

[13] R. Schwarz, W. Kuchen, Ber. 86, 1141 (1953).

[14] N. I. Gludina, Dissertation: "Photocolorimetric Determination of Silicon in Silicates and Organosilicon Compounds," D. I. Mendeleev Chem.-Tech. Inst., Moscow (1955).

[15] V. A. Klimova, M. O. Korshun and E. G. Bereznitskaya, J. Anal. Chem. (USSR) 11, 223 (1956). *

[16] V. A. Klimova, M. O. Korshun and E. G. Bereznitskaya, Proc. Acad. Sci. USSR 96, 287 (1954).

[17] A. P. Kreshkov and G. D. Nessonova, J. Anal. Chem. (USSR) 4, 220 (1949).

[18] A. P. Kreshkov, Yu. Ya. Mikhailenko and G. F. Yakimovich, J. Anal. Chem. (USSR) 9, 208 (1954).*

[19] M. Halmann and S. Pinchas, J. Chem. Soc. 1953, 626.

[20] L. W. Daasch, D. C. Smith, Anal. Chem. 23, 853 (1951).

[21] A. L. Geddes, J. Phys. Chem. 58, 1062 (1954).

Received October 29, 1956

D. I. Mendeleev
Chemical-Technological Institute,
Moscow

* Original Russian pagination. See C. B. Translation.

CATALYTIC DEHYDROGENATION OF ISOPENTENES INTO ISOPRENE

Yu. N. Usov, E. V. Skvortsova, N. I. Kuvshinova and L. A. Elovatskaya

A study of the catalytic dehydrogenation of pentanes and pentenes to isoprene has attracted many investigators [1-3]. However, the data published on this subject at the present time are extremely meager. The studies of N. I. Shuikin and co-workers [2-4] have been devoted to a search for efficient oxide catalysts for the dehydrogenation of n-pentane and isopentane to olefinic hydrocarbons.

The catalytic dehydrogenation of the isopentane fraction and of isoamylenes was investigated by Yu. G. Mamedaliev and co-workers [1, 5-7]. When the crude fraction was diluted with steam, the authors were able to obtain a comparatively small yield of isoprene on the commercial catalyst used for the dehydrogenation of butenes (24% in the catalyzate and 14-16%, based on the crude). Greater yields of diene hydrocarbons are obtained if the dehydrogenation is run under reduced pressure in the presence of chromium oxide catalysts. Under the optimum conditions, at a temperature of 630° and a pressure of 80 mm, Mavity and Zetterholm [8] were able to obtain a 33-35% yield of isoprene in one pass, and with recirculation – even up to 80% (based on the isoamylenes taken). The value of the interesting data obtained by these authors, showing that it is practical to dehydrogenate isopentane–isopentene mixtures to isoprene, is impaired somewhat due to the absence of details regarding the composition and method of preparing the catalyst used. It was shown by Grosse, Morrell and Mavity [9] that the position of the double bond in the starting isoamylene does not influence the isoprene yield.

In the present investigation we concentrated on the preparation and selection of an active contact for the transformation of isoamylenes into isoprene at atmospheric pressure, using nitrogen to dilute the vapors of the crude. The influence of the composition of the oxide catalyst on its dehydrogenation properties is shown in Table 1. An increase in the chromium oxide content or the addition of potash enhances the dehydrogenation ability of the catalysts. However, the larger (60%) Cr_2O_3 concentrations also favor an increase in carbon deposition, whereas K_2CO_3 reduces it in all cases. Consequently, it is most practical to use a catalyst with a low Cr_2O_3 content (8-10%) and K_2CO_3 as an additive.

Under the conditions of our experiments the use of a mixture of molybdenum trioxide and aluminum oxide, either as an independent contact or as an additive to an aluminum-chromium catalyst, proved to be impractical. Magnesium oxide is essentially without effect on the catalytic properties of an aluminum-chromium contact in the dehydrogenation of isoamylenes to isoprene. We will mention that, based on the data of N. I. Shuikin and co-workers [4], the presence of MgO in an aluminum-chromium catalyst facilitates the dehydrogenation of n-pentane. The favorable influence exerted by potash on the extent of dehydration of isoamylenes as established by us, is in harmony with the statement made by N. I. Shuikin and co-workers [2] relative to the composition of the optimum contact for the dehydrogenation of isopentane. On the other hand, based on the observation made by the above-cited authors the additions of potash reduce the activity of an oxide contact for the dehydrogenation of n-pentane. It seems to us that this different selectivity shown by magnesium oxide and potash toward extremely close reactions deserves further, more detailed study, which may possibly permit elucidation of the mechanism of their catalytic action.

The aluminum-chromium-potassium catalyst (No. 8), proving to the best for the preparation of isoprene, was prepared by us in accordance with the statement made by N. I. Shuikin and co-workers [2] relative to the composition of the optimum contact for the dehydrogenation of isopentane to isoamylenes. Consequently, this catalyst can be used to accomplish the dehydrogenation of isopentane to isoprene in two successive stages.

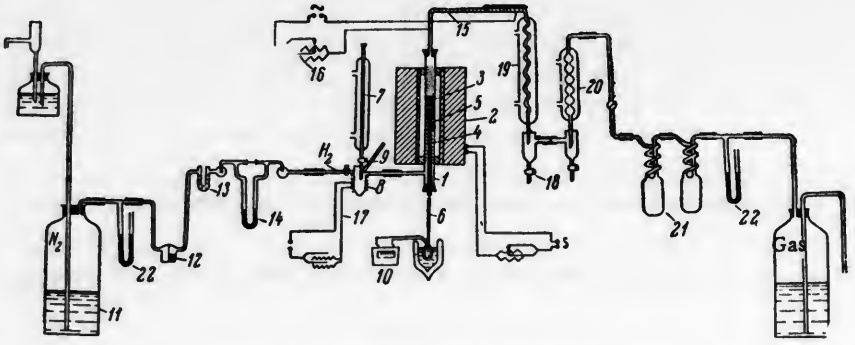


Diagram of the apparatus for the catalytic dehydrogenation of isoamylenes.
1) Quartz reactor, 2) electric tube furnace, 3) catalyst, 4) porcelain chips, 5) porcelain container, 6) thermocouple, 7) burette, 8) vaporizer, 9) thermometers, 10) galvanometer, 11) gasometer with pure nitrogen, 12) Tishchenko flask with H_2SO_4, 13) calcium chloride tube, 14) rheometer, 15) superheater, 16) autotransformer, 17) electrical winding of vaporizer, 18) receiver for liquid products, 19) coil condenser, 20) bulb condenser, 21) traps, 22) mercury manometer.

TABLE 1

Dehydrogenation Capacity of Oxide Catalysts as a Function of Their Composition (temperature 600°; v = 500 vol /vol. catalyst/hr ; $C_5H_{10} : N_2 = 1 : 7$. Experiment duration 30 minutes; catalyst amount 5 ml)

Catalyst Nos.	3	4a	14	15	13	8	5	10*	11*	9
Expt. Nos.	6	11	49	53	34	22	15	24	30	37
Catalyst composition (wt. %):										
Cr_2O_3	6	10	10	10	8	8.1	63	10	—	15
Al_2O_3	94	80	80	76	81	87.2	28	90	92	85
MoO_3	—	10	—	—	8	—	—	—	8	—
MgO	—	—	10	10	—	—	9	—	—	—
K_2CO_3	—	—	—	4	3	4.7	—	—	—	—
Material balance for the experiments:										
Amount of crude passed (in g)	4.08	3.95	3.98	3.91	3.98	3.44	4.01	3.22	3.98	3.93
Catalyzate (wt. %)	85.6	89.6	80.4	89.5	87.1	84.7	80.6	87.0	89.1	82.5
Gas (wt. %)	2.2	2.8	2.8	1.8	2.8	3.5	3.0	4.7	3.3	3.3
Carbon (wt. %)	7.3	8.8	6.8	1.8	5.8	4.6	10.9	4.8	5.8	7.1
Losses (wt. %)	4.9	—1.2	10.0	6.9	4.3	7.2	5.5	3.5	1.8	7.1
Amount of diolefinic hydrocarbons in the catalyzate (wt. %)	28	30	28	32	35	45	45	35	22	37
Yield of diolefinic hydrocarbons based on starting crude (wt. %)	24	27	22	29	30	38	36	30	19	30

*Commercial catalysts.

EXPERIMENTAL

The starting crude (a mixture of 2-methyl-1-butene and 2-methyl-2-butene in a 1 : 3 ratio; boiling range 30-39°, d_4^{20} 0.6581, n_D^{20} 1.3841) was isolated from the products of the catalytic dehydration of isoamyl alcohol by rectification through a column with an efficiency of 35 theoretical plates. Dehydrogenation of the isoamylenes was studied on nine different catalyst specimens, two of which (10 and 11) were commercial catalysts, while the others were prepared by us on chromium oxide and aluminum oxide as a base, and differed from each other in the ratios of the components and added promoters. The catalysts were prepared by the joint precipitation of the hydroxides of chromium, aluminum and magnesium by treatment of the nitrates of the latter in dilute solution with aqueous ammonia. The molybdic acid and potash were introduced into the catalyst by soaking . Conversion of the hydroxides to the corresponding oxides was effected by heating them in a stream of air at 550°. The compositions of the catalysts used in the present study are given in Table 1.

The experiments on the dehydrogenation of isoamylenes were run in an apparatus of the flow type (Figure), consisting of a quartz reactor (1) with catalyst (3), placed in an electric tube furnace (2). A chromel-alumel thermocouple (6) was used to measure the temperature in the catalyst zone. The crude was charged into the burette (7), having a volume of 25 ml and equipped with a cooling jacket. The pure nitrogen used as diluent was fed at a known rate into mixer (8), serving at the same time as a vaporizer for the isoamylenes. The reaction products were cooled in the coil and bulb condensers filled with broken glass packing (19 and 20) and then passed through two traps connected in series (21), which were immersed in a mixture of solid carbon dioxide and acetone (−80°). The gas was collected in the gasometer. Prior to experiment the catalyst was activated by the passage of hydrogen for 1-2 hours at 600°. The catalyst was regenerated by passing dry air over it at 600-630°.

For the liquid reaction products we determined the specific gravity, refractive index, molecular weight based on the vapor density [10, 11], bromine number [12], and amount of diolefinic hydrocarbons with a conjugated system of double bonds [13]. The gas was analyzed using the apparatus developed by the VTI [All-Union Heat Engineering Institute] [14]. The amount of carbon on the catalyst was calculated from the amount of CO_2 and CO in the gas after regeneration of the catalyst.

A series of 3 to 4, and at times even more, experiments was run with each catalyst specimen under constant conditions. The more typical of the performed experiments are given in Table 1. All of the catalysts tested failed to show cracking properties and proved to be quite selective. The gas obtained as the result of dehydrogenation contained 95-100% hydrogen. The presence in the gas of a small amount (2-5%) of tertiary and secondary unsaturated hydrocarbons is considered to be due to the presence of the vapors of pentenes and isoprene, brought about by the nitrogen. The dehydrogenation process was accompanied by a noticeable deposition of carbon on the catalyst (5-10%) and a very slight formation of tarry products.

As can be seen from the data in Table 1, increasing the amount of chromium oxide in the catalyst from 6 to 63% results in a 17% increase in the concentration of isoprene in the catalyzate. Approximately the same effect is obtained with a relatively small expenditure of chromium oxide by adding about 5% of potash (catalysts 3 and 8). A smaller, but still favorable influence, is shown by the addition of 3-4% K_2CO_3 to the catalysts containing MoO_3 and MgO (catalysts 4a and 13, 14 and 15). The commercial chromium catalysts (10) gives somewhat better results than does the laboratory specimen 3, but still is markedly inferior to catalyst 8. On the commercial molybdenum catalyst (11), containing 8% MoO_3, the total yield of isoprene was only 19%. The addition of 10% MoO_3 to the aluminum-chromium contact is without essential effect on the dehydrogenation capacity of the latter (catalysts 3 and 4a). The presence of MoO_3 in the aluminum-chromium-potassium catalyst even lowers the activity of the latter (catalysts 8 and 13). From a comparison of the results, obtained with catalysts 3 and 14, it follows that MgO does not change the properties of the aluminum-chromium contact, while its addition to the aluminum-chromium-potassium catalyst sharply lowers the dehydrogenation capacity of the latter.

Under the conditions of our experiments the best in the sense of dehydrogenation capacity proved to be catalysts 5 and 8, but due to the substantial deposition of carbon obtained with catalyst 5 preference should be given to specimen 8, which, possessing the same dehydrogenation capacity as specimen 5, gives one half as much carbon. Catalyst 8 was subjected to a more careful study. It was established that the degree of carbon

TABLE 2

Results of Experiments on the Dehydrogenation of Isopentenes Over Catalyst 8 (experimental conditions: 600°; v = 500 vol /vol. catalyst/hr ; $C_5H_{10} : N_2 = 1 : 7$)

Expt. Nos.	Characteristics of the catalyzate					Yield of diolefinic hydrocarbons based on crude (in wt. %)
	d_4^{20}	n_D^{20}	bromine number	molecular weight	concentration of diolefinic hydrocarbons in catal.	
19	0.6656	1.4012	250	69	46	35
20	0.6694	1.4038	257	68	40	32
21	0.5674	1.4020	263	71	44	35
22	0.6652	1.3999	264	69	38	32
48 *	—	1.3990	—	—	37	28

*Expt. 48 was run after regeneration of the catalyst, having operated continuously for 150 minutes.

deposition on the catalyst decreases as the length of the experiment is increased, but at the same time the yield of diolefinic hydrocarbons decreases. Consequently, the length of the operating period, during which the catalyst fails to show material decrease in activity, constitutes 30-60 minutes. As can be seen from the data in Table 2, catalyst 8 fully assures a satisfactory reproducibility of results in a series of experiments (Expts. 19-22) and even after long continuous operation (Expt. 48).

A study of the dependence of the degree of dehydrogenation on the basic parameters of the process revealed that increasing the dilution of the crude with nitrogen by a factor of 1.5-2 is practically without effect on the yield of diolefinic hydrocarbons or on the extent of carbon desposition on the catalyst. Increasing the temperature from 600 to 640° leads to a sharp reduction in the yield of catalyzate (from 80 to 60%) and to an increase in the concentration of diolefinic hydrocarbons in it (from 47 to 58%). However, here the yield of diolefinic hydrocarbons calculated on the crude remains essentially unchanged. Both coke formation (from 4 to 12%) and tar formation show substantial increase. A 2-fold increase in the space velocity, although it reduces carbon deposition (from 5 to 1.5%), at the same time also substantially reduces the yield of isoprene.

In conclusion it is necessary to mention that the data obtained by us on the catalytic dehydrogenation of isoamylenes, both relative to the concentration of dienic hydrocarbons in the catalyzate (35-45%), and relative to their yield based on the starting crude (30-35%), are in no way inferior to the results obtained in a vacuum in study [8]. Thus, for example, Mavity and Zetterholm [8] at 630° and a pressure of 80 mm obtained in one pass a 35% yield of diolefinic hydrocarbons with their concentration in the C_5 fraction being 38%.

At the present time the obtained catalyzates are being developed by us to isolate isoprene.

SUMMARY

1. We tested the activity of nine different oxide catalyst specimens with respect to the dehydrogenation of isoamylenes at a temperature of 600°, a space velocity for the vapors of the hydrocarbons of 500 vol /vol. catalyst/hr , and a 7-fold dilution with nitrogen.

2. It was established that the addition of potash enhances the dehydrogenation capacity of the catalysts and reduces coke formation. The introduction of molybdenum trioxide, and also of magnesium oxide, is without essential effect on the dehydrogenation properties of an aluminum-chromium catalyst.

3. The best dehydrogenation catalyst for the preparation of isoprene is an aluminum-chromium-potassium contact.

LITERATURE CITED

[1] Yu. G. Mamedaliev, M. A. Dalin and A. Z. Shikhmamedbekova, Proc. Acad. Sci. Azerbaidzhan SSR 11, 811 (1955).

[2] N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva and Yu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 952.*

[3] N. I. Shuikin and E. A. Timofeeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 567.*

[4] E. A. Timofeeva, S. S. Novikov and N. I. Shuikin, Proc. Acad. Sci. USSR 92, 345 (1953).

[5] Yu. G. Mamedaliev and M. A. Dalin, Proc. Acad. Sci. Azerbaidzhan SSR 11, 14 (1955).

[6] Yu. G. Mamedaliev, M. A. Dalin and T. I. Mamedov, Trans. Inst. Chem., Acad. Sci. Azerbaidzhan SSR 15, 106 (1956).

[7] M. A. Dalin and A. Z. Shikhmamedbekova, Trans. Inst. Chem., Acad. Sci. Azerbaidzhan SSR 15, 84 (1956).

[8] J. M. Mavity, E. E. Zetterholm, Trans. Am. Inst. Chem. Engrs. 40, 473 (1944).

[9] A. V. Grosse, J. C. Morrell, J. M. Mavity, Ind. Eng. Ch. 32, 309 (1940).

[10] B. M. Rybak, Analysis of Petroleum and Petroleum Products, Azneftizdat [State All-Union Trust of the Azerbaidzhan Oil and Gas Industry Press] (1948).**

[11] Methods of Technical Analysis Used in the Synthesis of Hydrocarbon Fuels, Gostoptekhizdat [State Scientific and Technical Press of Petroleum and Mineral Fuel Literature] (1941).**

[12] G. D. Galpern, Trans. Petroleum Inst., Acad. Sci. USSR 4, 116 (1954).

[13] H. P. Kaufmann, J. Baltes and H. Buter, Ber. 70, 903 (1937).

[14] M. I. Dementyeva, Analysis of Hydrocarbon Gases, Gostoptekhizdat (1953).**

Received September 24, 1956

Saratov State University

*Original Russian pagination. See C. B. Translation.
**In Russian.

ACETONATION OF HIGHER ALIPHATIC DIHYDROXY ACIDS

P. A. Artamonov

The first investigations devoted to a study of the reaction between acetone and polyhydroxy compounds were made by Schiff [1]. Slightly later this reaction was used by Fischer [2] to obtain individual acetone compounds with various carbohydrates (monoses, hexitols, etc.) and glycerine.

Acetone derivatives were used by V. I. Esafov [3] to study the structure of dihydroxy acids. The experiments of Esafov on the acetonation of dihydroxystearic acids were repeated by I. P. Kuranova [4], who obtained similar results.

In the opinion of Esafov, the large difference in the yields of the acetone compounds of dihydroxystearic acids is related to the position of the hydroxyl groups in the latter, and specifically, in the acid with m. p. 95° the hydroxyl groups are found in the cis-position, whereas in the corresponding isomeric acid with m. p. 132° the hydroxyl groups are found in the trans-position.

It seemed very interesting to us to trace the course of the acetonation of the racemates of the 2,3- and 6,7-dihydroxystearic acids, and also those of the 2,3- and 13,14-dihydroxybehenic acids.

The study made by us of the process for the acetonation of the indicated dihydroxy acids supported the opinion [3] expressed in the literature, namely, that the racemates of diastereoisomers condense to a different degree with acetone. Thus, the low-melting 6,7-dihydroxystearic acid with m. p. 115°, obtained from the oxidation of petroselaidic ($\Delta^{6,7}$-trans-octadecenoic) acid, reacted with acetone to the extent of 80%, while the high-melting 6,7-dihydroxystearic acid with m. p. 122°, obtained from the oxidation of petroselinic ($\Delta^{6,7}$-cis-octadecenoic) acid, under identical conditions reacted with acetone to the extent of only 9.59%.

A similar relationship is also observed in the condensation of the 13,14-dihydroxybehenic acids. The low-melting dihydroxybehenic acid with m. p. 101°, obtained from the oxidation of brassidic ($\Delta^{13,14}$-trans-docosenoic) acid, reacted with acetone to the extent of 33.9%, while the high-melting acid with m. p. 133°, obtained from the oxidation of erucic ($\Delta^{13,14}$-cis-docosenoic) acid, reacted with acetone only to the extent of 5.5%.

In addition, it was established that the reactivity of the higher aliphatic dihydroxy acids in their condensation with acetone is strongly dependent on the location of the hydroxyl groups with respect to the carboxyl group. Thus, 6, 7-dihydroxystearic acid readily condenses with acetone, forming isopropylidene-6,7-dihydroxystearic acid in 80% of the theoretical yield, while the 2,3-dihydroxystearic acid under the same conditions was completely inert toward acetone.

A similar picture is also observed in the condensation of the 2,3- and 13,14-dihydroxybehenic acids. Thus 13,14-dihydroxybehenic acid reacted with acetone to the extent of 33.9%, while the 2,3-dihydroxybehenic acid was completely unreactive.

Consequently, the reactivity of a dihydroxy acid in its condensation with acetone decreases as the hydroxyl groups shift toward the carboxyl group, and when the hydroxyl groups are located between the second and third carbon atoms from the carboxyl group, the dihydroxy acid is incapable of condensation with acetone under the indicated conditions.

In addition, the size of the dihydroxy acid molecule also apparently exerts an influence on its reactivity relative to condensation with acetone. Thus, 6,7-dihydroxystearic acid (C_{18}) reacted with acetone to the extent of 80%, while 13,14-dihydroxybehenic acid (C_{22}) under the same conditions reacted only to the extent of 33.9%. Consequently, the reactivity of a dihydroxy acid in its condensation with acetone decreases as the molecular weight increases.

EXPERIMENTAL

Preparation of Higher Aliphatic Dihydroxy Acids. The dihydroxy acids needed for the acetonation studies were obtained by the A. M. Zaitsev method [5], i.e., by the potassium permanganate oxidation of the following acids acids: $\Delta^{2,3}$-trans-octadecenoic (m. p. 59°), $\Delta^{6,7}$-cis-octadecenoic (petroselenic) (m. p. 30°), $\Delta^{6,7}$-trans-octadecenoic (petroselaidic) (m. p. 53°), $\Delta^{2,3}$-trans-docosenoic (m. p. 70.5°), $\Delta^{13,14}$-cis-docosenoic (erucic) (m. p. 33.5°) and $\Delta^{13,14}$-trans-docosenoic (brassidic) (m. p. 60°) acids.

As the result of oxidizing the indicated acids,we obtained the following dihydroxy acids: 2,3-dihydroxystearic (m. p. 126.5°), 6,7-dihydroxystearic, low-melting form, corresponding to the oxidation of petroselaidic acid (m. p. 115°), 6,7-dihydroxystearic, high-melting form, corresponding to the oxidation of petroselinic acid (m. p. 122°), 2,3-dihydroxybehenic (m. p. 129°), 13,14-dihydroxybehenic, low-melting form, corresponding to the oxidation of brassidic acid (m. p. 101°), and 13,14-dihydroxybehenic acid, high-melting form, corresponding to the oxidation of erucic acid (m. p. 133°).

Acetonation of Higher Aliphatic Dihydroxy Acids. We ran the acetonation of the obtained dihydroxy acids by the following method: 2 g of the acid was placed in a small flask with well-fitting ground-glass stopper, 20 ml of chemically pure anhydrous acetone containing 0.0986 g of gaseous hydrogen chloride was added, and after the acid had dissolved the solution was allowed to stand at room temperature for 10 days. At the end of this time the flask contents were transferred to a porcelain dish, and the acetone was evaporated at room temperature; the residue was an oily liquid, containing a small amount of water and some crystals of unreacted dihydroxy acid. To separate it from impurities the oily liquid was dissolved in 30 ml of petroleum ether (35-45°); here a portion of the precipitate failed to dissolve and it was separated from the liquid by filtration through ordinary filter paper. The petroleum ether solution was shaken with activated carbon, filtered, and dried over fused sodium sulfate. Then the solution was filtered again, and the petroleum ether was evaporated at room temperature. The residue of isopropylidene compound, obtained from the evaporation, was freed from solvent by drying in a vacuum (0.5 mm) to constant weight, and then analyzed.

The acetonation of 2 g of the low-melting 6,7-dihydroxystearic acid with m. p. 115° gave us 1.88 g (80%) of isopropylidene-6,7-dihydroxystearic acid, previously unknown.

d_4^{15} 0.9529, n_D^{15} 1.4590, MR 102.75; calc. 102.84.

Found %: C 71.03, 70.16; H 11.49, 11.59. M 364.3, 358.94. $C_{21}H_{40}O_4$. Calculated %: C 70.70; H 11.32. M 356.3.

In appearance the obtained isopropylidene derivative is a clear, almost colorless oily liquid with a scarcely preceptible odor. The substance hydrates with difficulty. Thus, we were able to obtain the starting 6,7-dihydroxystearic acid only by prolonged (6 hours) boiling of the isopropylidene derivative with water, acidulated with sulfuric acid.

In the acetonation of the high-melting 6,7-dihydroxystearic acid with m. p. 122° the yield of isopropylidene-6,7-dihydroxystearic acid was only 9.59%. Thus, from 4 g of 6,7-dihydroxystearic acid we obtained only 0.43 g of the acetone derivative (n_D^{15} 1.4589). The remainder of the dihydroxy acid failed to react with the acetone.

Found %: C 70.82, 70.39; H 11.44, 11.50. Neutralization equiv. 157.3, 156.71. $C_{21}H_{40}O_4$. Calculated %: C 70.72; H 11.32. Neutralization equiv. 157.5.

It should be mentioned that under the indicated conditions the 2,3-dihydroxystearic acid with m. p. 126° completely failed to react with acetone.

In connection with this it was decided to change the method of acetonation by increasing the time of holding the reactant mixture to 20 days and the concentration of the condensation agent (HCl) to 0.5133 g per 2 g of dihydroxy acid. However, we were unable to obtain reaction even under these conditions.

The acetonation of the low-melting 13,14-dihydroxybehenic acid with m. p. 101° proceeded with greater difficulty than was the case with the low-melting 6,7-dihydroxystearic acid. From 2 g of the dihydroxy acid we obtained only 0.75 g (33.9%) of isopropylidene-13,14-dihydroxybehenic acid (n_D^{15} 1.4480), previously unknown.

Found %: C 73.00, 72.78; H 11.80, 11.78. Neutralization equiv. 123.6, 135.8. $C_{25}H_{48}O_4$. Calculated %: C 72.78; H 11.75. Neutralization equiv. 136.1.

The high-melting 13,14-dihydroxybehenic acid with m. p. 133° condenses with even greater difficulty with acetone. From 2 g of the dihydroxy acid we were able to isolate only 0.12 g (≈5.5%) of the acetone derivative.

The 2,3-dihydroxybehenic acid, like the acetone 2,3-dihydroxystearic acid, completely failed to react with aceton under the adopted conditions.

SUMMARY

1. It was shown that the ability of dihydroxy acids to condense with acetone depends on both the spatial arrangement of the hydroxyl groups in the acid and on their distance from the carboxyl group.

2. The dihydroxy acids, obtained by the oxidation of unsaturated aliphatic acids with a trans-configuration, show more complete condensation with acetone than do the dihydroxy acids, obtained by the oxidation of aliphatic acids with a cis-configuration.

3. The ability of a dihydroxy acid to condense with acetone decreases with increase in the molecular weight.

LITERATURE CITED

[1] H. Schiff, Lieb. Ann, 244, 19 (1888).

[2] E. Fischer, Ber. 28, 1145 (1895); Ber. 53, 1889 (1920).

[3] V. I. Esafov, J. Gen. Chem. 6, 1818 (1936).

[4] I. P. Kuranova, Dissertation: "Investigation of the Oxides of Higher Aliphatic Unsaturated Acids," Leningrad State University (1953).*

[5] A. M. Zaitsev, J. Russ. Chem. Soc. 17, 417 (1885).

Received September 27, 1956

All-Union Scientific Research Institute of Fats

* In Russian.

IMINES OF DI- AND POLYKETONES

II. TRISINDANDIONE

G. Ya. Vanag and G. Ya. Dubur

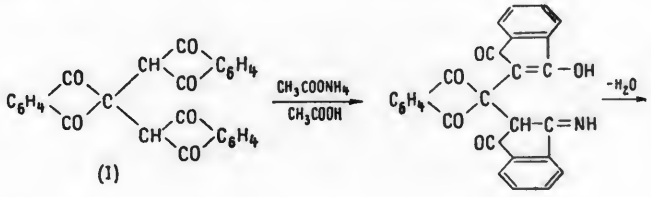
In previous studies [1, 2] it had been shown that the 2-substituted 1,3-indandiones are easily iminated when reacted with ammonium acetate in glacial acetic acid, in which connection the oxygen atom of one carbonyl group is replaced by the imino group.

It was interesting to determine how compounds containing two or more indandione groups in the molecule would behave. For this we selected the rather easily available trisindandions (I) [3]. Since this compound contains three indandione groups, then it could be expected that the triimine would be formed, but since indandione itself, not having an unsubstituted hydrogen in the methylene group, does not react with ammonium acetate [2], then it would be more probable to expect the formation of the diimine.

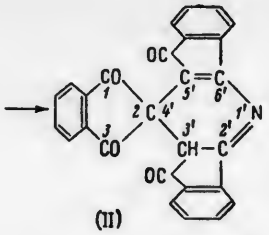
If trisindandione is heated with ammonium acetate in glacial acetic acid, then the white substance is easily converted to a reddish-brown material. The latter is very slightly soluble in glacial acetic acid, and consequently coats the unreacted trisindandione, for which reason it is difficult to make the reaction complete. Consequently, to obtain the pure substance it is best to first dissolve the trisindandione in boiling glacial acetic acid and only after this to add the ammonium acetate.

Judging from the nitrogen content, the reaction product is the monoimine of trisindandione. In order to obtain the diimine, the reaction was run for a longer time, the trisindandione was added in small portions to a boiling mixture of ammonium acetate in glacial acetic acid, the prepared "monoimine" was heated with a large excess of ammonium acetate, etc. However, in all cases the main product isolated was the "monoimine." Compounds with a higher nitrogen content were also isolated in small amounts as by-products; however, the nitrogen content never reached that of the "diimine"; the obtained products crystallized with difficulty and were not isolated in completely pure form. They could have also been formed by the cleavage of one indandione group during reaction, which phenomenon had already been mentioned earlier [3, 4]. The chemical nature of these by-products has not yet been determined.

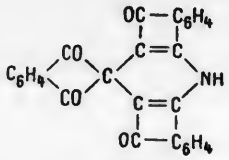
In its properties the "monoimine" of trisindandione is quite different from all of the other investigated imines of β-diketones. Its nitrogen is bound very firmly and is not cleaved by treatment of the "monoimine" with either acids or alkali. or by reduction under various conditions, or even by fusion with caustic alkali. Reduction of the "monoimine" does not give a compound with a primary amino group. All of this indicates that the imine, even if it were initially formed, immediately underwent further transformations. It is most probable that its imino group (or enamine group) condensed further with the enolic form of a second indandione group, closing the pyridine ring with the formation of 1,3-indandionespiro-(2,4')-2',3',6',5'-dibenzoylene-3', 4'-dihydropyridine (II).



(I)



(II)

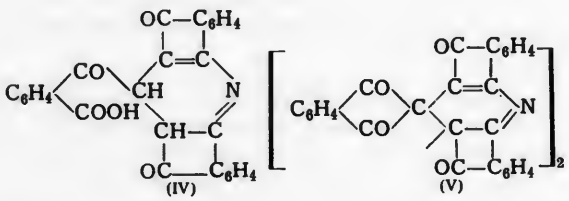


(III)

Examples of a similar cyclization are described in the literature. For example, quite recently it was shown [5] that the reaction product of p-benzoquinone with the imine of acetylacetone easily cyclizes into an indole derivative.

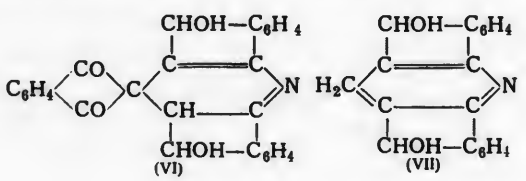
To be sure, it is also possible for both of the enolic groups in trisindandione to react immediately with ammonium acetate; in such a case it is not the 3',4'-dihydropyridine derivative (II) that is obtained, but the 1',4'-dihydropyridine derivative (III). But this compound, containing a hydrogen on the nitrogen, should give both the nitroso and the acetyl derivative, which is not observed, and consequently formula (II) must be considered to be the more valid. This formula contains an enolizable hydrogen, and actually compound (II) dissolves in alkali, forming a green solution. To be sure, a compound with an enolizable hydrogen could have also been formed by the cleavage of the phthaloyl group (IV) with alkali, which is frequently observed for an indandione group. In support of the premise that such cleavage does not occur in the given case is the fact that compound (II) also dissolves with the same green color in anhydrous piperidine, where cleavage of the indandione ring is impossible.

Consequently, an enolizable hydrogen is contained in the compound itself, which lends support to formula (II).



(IV) (V)

Acidification of either the alkaline or of the piperidine solution causes the green color to disappear, and the original product is again obtained as a precipitate. The green color of these solutions gradually disappears also with their long standing in an open dish, in which connection a yellow precipitate is deposited. The disappearance of the green color begins with the top layer of the solution and then steadily migrates downward, from which it follows that here we have oxidation by atmospheric oxygen. This process can be made to proceed much faster by the addition of hydrogen peroxide or other oxidizing agents. The yellow oxidation product is already insoluble in alkali, from which it follows that the oxidation process is linked with the enolizable hydrogen. It is possible for an active hydrogen to be converted into a hydroxyl group, similar to the case where trisindandione under comparable conditions is oxidized to hydroxytrisindandione [6]. However, we were unable to show the presence of a hydroxyl group in the oxidation product. Consequently, only a second possibility remains, namely, that the oxidation proceeds with removal of the active hydrogen and dimerization of the molecule (V). Since the oxidation product is practically insoluble in the ordinary organic solvents, we have as yet been unable to determine its molecular weight.



(VI) (VII)

When compound (II) and its oxidation product (V) are heated in glacial acetic acid with zinc dust both substances go into solution. White reaction products were isolated from the solutions, which products were different from each other neither being a primary amine. The product obtained by the reduction of compound (II) shows a violet fluorescence in glacial acetic acid solution. It is possible that the carbonyl groups of the benzoylene groups are reduced to alcohol groups (VI). Thus, for example, Errera [7] in the reduction of dibenzoylenepyridine (α-diphenylpyridine diketone) under the same conditions obtained the dihydroxy derivative (VII), which in glacial acetic acid also gives the same violet fluorescence. This, if only indirectly, supports the validity of the reaction scheme proposed by us and the structure of the obtained products. A study of the reduction products is being continued.

The reaction described by us is somewhat reminiscent of the Hantzsch reaction – the preparation of pyridine derivatives from δ-diketones. Starting with methenylbisindandione, Errera obtained the already mentioned α-diphenylpyridine diketone in this manner. Since trisindandione is at the same time also a δ-diketone, then the reason for the formation of the pyridine derivative in our case becomes clear.

As a result, starting with trisindandione, it is possible by reacting it directly with ammonium acetate to easily pass over to extremely complex polycyclic derivatives of pyridine.

EXPERIMENTAL

1,3-Indandionespiro-(2,4')-2',3',6',5'-dibenzoylene-3',4'-dihydropyridine (II). One gram of trisindandione in 100 ml of glacial acetic acid was heated to boiling, 5 g of ammonium acetate was added and the mixture boiled 3 hours. The liquid first assumed a brown, and then a dark red color; glistening red crystals appeared in the liquid. They were suction-filtered and boiled twice with 25 ml of glacial acetic acid to remove any more soluble by-products of the reaction, and then twice with 5-10% ammonia in order to remove any traces of unreacted trisindandione, which is readily soluble in ammonia. The yield of 1,3-indandionespiro-(2,4')-2',3',6',5'-dibenzoylene-3',4'-dihydropyridine was about 0.8 g (80%). Fine red-brown tetragonal plates with a violet tinge. M. p. 285° (block).

Found %: N 3.32, 3.38. $C_{27}H_{13}O_4N$. Calculated %: N 3.37.

The compound is very difficultly soluble in the ordinary organic solvents, and somewhat more readily soluble in pyridine and benzyl alcohol, but it fails to crystallize from them on cooling. In concentrated sulfuric acid it dissolves even in the cold with a green color, and when diluted with water, a precipitate of the unchanged substance is obtained. When its solution in concentrated sulfuric acid is heated, the solution turns yellow and when diluted with water, gives a yellow precipitate containing a higher amount of nitrogen than the starting substance. The compound is insoluble in hydrochloric acid; when heated with nitric acid it is converted into a yellow substance (oxidation product). With prolonged shaking the substance dissolves with a green color in dilute sodium hydroxide, more rapidly when heated, but soon a yellow precipitate begins to deposit. The compound dissolves rapidly in alcoholic alkali or in alcoholate solution, forming an emerald-green solution, and it dissolves in piperidine with a blue-green color. It dissolves in nitrobenzene when heated, but at the same time it also reacts, forming a green solution; we are of the opinion that here oxidation of (II) occurs, and the reduction of nitrobenzene to nitrosobenzene. The unchanged substance crystallizes out from acetic anhydride even after long boiling.

Oxidation. 1) Substance (II) was suspended in alcohol and an aqueous solution of potassium hydroxide was added. This gave a blue-green solution. The solution on standing turned yellow, beginning from the top layer; when shaken the whole solution rapidly turned yellow, and the yellow oxidation product (V) was obtained as a precipitate.

Found %: N 3.15. $C_{54}H_{24}O_8N_2$. Calculated %: N 3.38.

2) A solution of 1.5 g of substance (II) in 50 ml of 0.5% methanolic potassium hydroxide solution was prepared, 2 ml of 30% hydrogen peroxide was added and the mixture heated on the water bath. The original green color of the solution faded and a yellow precipitate was obtained. After 1 hour the whole mixture had a bright yellow color. The precipitate was recrystallized from either acetic anhydride or concentrated nitric acid. Long thin yellow needles. M. p. 355° (block) with decomposition.

Found %: N 3.65 (from acetic anhydride), 3.45 (nitric acid). $C_{54}H_{24}O_8N_2$. Calculated %: N 3.38.

The substance is very slightly soluble in the ordinary organic solvents, and somewhat more soluble when boiled in acetic anhydride, benzyl alcohol or pyridine. It dissolves in concentrated sulfuric acid with an orange-yellow color. It is not appreciably soluble in alcoholic alkali even when boiled, and the color of the solution does not change.

Reduction. Substance (II) in glacial acetic acid was heated with zinc dust until the solution became colorless and then the hot solution was filtered. The filtrate had a yellow color with a violet fluorescence. The filtrate was diluted with water, filtered, and the filtrate treated with a large excess of ammonia. This gave a white flocculent precipitate of (VI).

Found %: N 3.39. $C_{27}H_{15}O_4N$. Calculated %: N 3.35.

SUMMARY

The reaction of trisindandione with ammonium acetate in glacial acetic acid gave 1,3-indandionespiro-(2,4')-2',3',6',5'-dibenzoylene-3',4'-dihydropyridine. A mechanism for the reaction was given. As a result, starting with trisindandione, it is an easy matter to pass over to extremely complex polycyclic derivatives of pyridine.

LITERATURE CITED

[1] G. Vanag and E. Vanag, Bull. Acad. Sci. Latvian SSR 9, (86), 137 (1954).

[2] G. Ya. Vanag, Ya. F. Freimanis and G. F. Zakis, J. Gen. Chem. 27, 2509 (1957).*

[3] C. Liebermann, L. Flatow, Ber. 33, 2435 (1900).

[4] G. Ya. Vanag and L. S. Geita, J. Gen. Chem. 26, 511 (1956).*

[5] A. N. Grinev, V. I. Shvetsov and A. P. Terentyev, J. Gen. Chem. 26, 1449 (1956).*

[6] C. Liebermann, J. Landau, Ber. 34, 2149 (1901); A. Hantzsch, W. Fischer, Lieb. Ann. 392, 328 (1912).

[7] G. Errera, Gazz. 32, II, 330 (1902); 33, I, 417 (1903).

Received October 12, 1956

Latvian State University

*Original Russian pagination. See C. B. Translation.

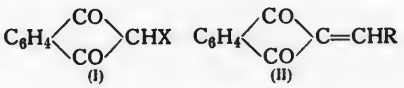
IMINES OF DI- AND POLYKETONES

III. BENZALINDANDIONE

G. Ya. Vanag, E. I. Stankevich and E. Ya. Gren

Indandiones of type (I), where X is atyl, alkyl, nitro group, etc., react readily with ammonium acetate in glacial acetic acid [1-3], in which connection the oxygen of one of the carbonyl groups is replaced by the imino group. With indandiones, in which both of the active hydrogens of the methylene group are substituted, it has been impossible up to now to obtain ketimines by this method.

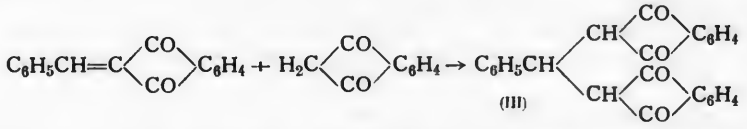
It was interesting to determine how compounds of type (II), not having an active hydrogen, but containing a double bond at carbon 2, would behave in this reaction. Such indandiones are obtained by the reaction of 1,3-indandione with aldehydes [4, 5]. The reaction proceeds so easily with aromatic aldehydes that it has even been proposed to use indandione for the identification of this class of aldehydes. As an example we selected benzal-indandione (II, R = C_6H_5).



(I) (II)

If benzalindandione in glacial acetic acid is heated with excess ammonium acetate, then the solution turns dark red, and after some time a yellow crystalline precipitate deposits. If hydrogen peroxide is added to the red filtrate and the mixture heated, then the liquid becomes colorless and again crystals of the same yellow substance are obtained. It is easily purified by recrystallization.

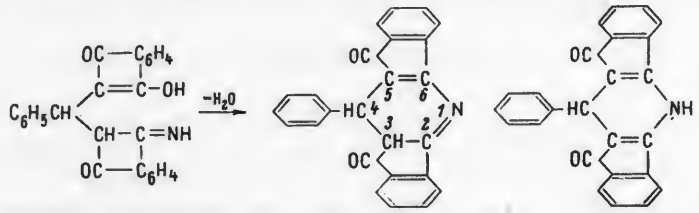
Analysis of the obtained compound revealed that it contains 1 nitrogen atom for approximately 1.5 molecules of the benzalindandione. It is obvious that during imination the benzalindandione suffered cleavage and that the unknown cleaved portion added to the uncleaved molecule. It is known that benzalindandione is not only easily formed from indandione and benzaldehyde, but that it also undergoes cleavage into the starting components, especially under the influence of alkali. Such cleavage may also occur when benzalindandione is heated with ammonium acetate, in which connection one of the components can add to the benzalindandione or to its imination product. In order to determine whether it is indandione or benzaldehyde that adds, a similar reaction was run with m-nitrobenzalindandione. Here, the same as with benzalindandione, a yellow substance was obtained, but containing 2 nitrogen atoms per 1.5 molecules of the nitrobenzalindandione. From this the mechanism of the given reaction became clear. Benzalindandione during the course of the reaction is partially cleaved into indandione and benzaldehyde. Indandione at the moment of its formation immediately adds to the uncleaved benzalindandione, forming phenyldiindandionylmethane (III).



(III)

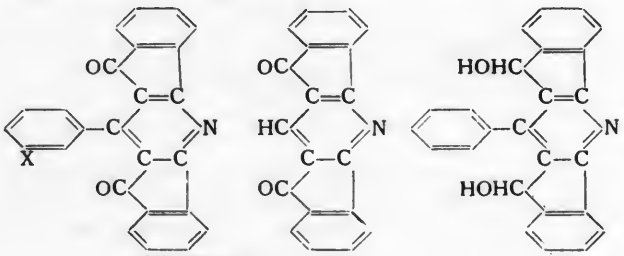
That indandione can actually add to the active double bond of indandionylene derivatives had already been shown earlier by one of us together with L. S. Geita [6]. The results of a systematic study of the addition of indandione to arylideneindandiones will be given in a separate paper.

The formed phenyldiindandionylmethane (III) already contains an active hydrogen in the indandione groups and consequently can be iminated "normally ". And here, the same as in the previous case with trisindandione [3], we obtain not the desired diimine, but only the "monoimine." This "monoimine" proves to be a very stable compound and does not hydrolyze, i.e., it fails to lose nitrogen when boiled with acids or alkalies. It does not give a primary amine on reduction. It is obvious that here also cyclization of the initial imine (IV) occurred with the formation of 4-phenyl-2,3,6,5-dibenzoylenedihydropyridine (V).



(IV) (V) (VI)

And here, the same as in the case of trisindandione [3], it is theoretically possible for both the 3,4- (V) and 1,4-dihydropyridine (VI) to be formed. The obtained compound is extremely unstable, readily oxidizes in the air, and could not be isolated in the pure state. But the fact that it dissolves in alkalies with a dark green color suggests that an enolizable hydrogen is present, and consequently, speaks in favor of formula (V). Both dihydropyridines on oxidation can give the same substance, namely 4-phenyl-2,3,6,5-dibenzoylene pyridine (VII). In a similar manner m-nitrobenzalindandione gave 4-m-nitrophenyl-2,3,6,5-dibenzoylenepyridine (VIII).



(VII) X = H;
(VIII) X = NO_2 (IX) (X)

2,3,6,5-Dibenzoylenepyridine (IX), obtained by Errera [7] by reacting methenylbisindandione with ammonium hydroxide, is described in the literature; in its properties it is extremely close to the product obtained by us.

The solitary functional groups in compound (VII) are carbonyl groups. Their presence was shown by preparing the disemicarbazone, monoxime and dioxime. The oximes are soluble in alkalies. The acetyl derivative of the monoxime was also prepared.

Treatment of compound (VII) with zinc dust in glacial acetic acid resulted in reduction of both of the carbonyl groups to hydroxyls with the formation of compound (X), in which connection the solution showed a violet fluorescence. The hydroxyl groups in compound (X) were shown by preparing the bis-phenylisocyanate. In the reduction of the structurally similar dibenzoylenepyridine (IX) Errera observed [8] the same violet fluorescence, in which connection both carbonyl groups in (IX) were reduced to alcohol groups.

As a result, starting with the easily obtainable benzalindandione, it is possible by its simple reaction with ammonium acetate to pass over to complex polycyclic pyridine compounds.

EXPERIMENTAL

4-Phenyl-2,3,6,5-dibenzoylenepyridine (VII). A mixture of 5 g of benzalindandione, 20-30 g of ammonium acetate and 30 ml of glacial acetic acid was boiled in a flask under reflux for 30 minutes. The liquid assumed a dark-red color and yellow crystals appeared in it. The hot solution was filtered and the crystals on the filter were washed with glacial acetic acid. The filtrate was treated with 3-4 ml of perhydrol and then warmed

slightly. The solution became light orange. The precipitate obtained here and the first crystals, found on the filter, was recrystallized from either benzene or toluene. The yield of 4-phenyl-2,3,6,5-dibenzoylenepyridine was 2.5 g (62%). M. p. 354-355° (block).

Found %: N 4.08, 4.02. M 370 (Rast). $C_{25}H_{13}O_2N$. Calculated %: N 3.90. M 359.

4-(m-Nitrophenyl)-2,3,6,5-dibenzoylenepyridine (VIII). A mixture of 4.2 g of m-notrobenzalindandione, 20 g of ammonium acetate and 70 ml of glacial acetic acid was boiled under reflux for 20 minutes and then worked up in the same manner as in the preceding example. The obtained 4-(m-nitrophenyl)-2,3,6,5-dibenzoylenepyridine was recrystallized from either toluene or xylene. Yield 1.8 g (56%); the compound decomposes without melting at around 390° (block).

Found %: N 6.62. $C_{25}H_{12}O_4N_2$. Calculated %: N 6.89.

4-Phenyl-2,3,6,5-dibenzoylenepyridine Disemicarbazone. 4-Phenyl-2,3,6,5-dibenzoylenepyridine in pyridine solution was heated on the water bath with semicarbazide hydrochloride. The yellow crystals were washed with dioxane, in which they are very slightly soluble; we were unable to recrystallize them. When heated they decompose without melting.

Found %: N 20.21. $C_{27}H_{19}O_2N_7$. Calculated %: N 20.72.

Oximation of 4-Phenyl-2,3,6,5-dibenzoylenepyridine. A mixture of 1 g of 4-phenyl-2,3,6,5-dibenzoylenepyridine, 20 ml of pyridine and 0.1 g of hydroxylamine hydrochloride (1 equiv.) was heated for several hours on the water bath and then poured into 100 ml of hydrochloric acid (1:1). This gave a pale yellow flocculent precipitate. The compound was purified by dissolving in alkali, filtering, and again precipitating with hydrochloric acid. Yellow crystals after recrystallization from dioxane, consisting mostly of the monoxime. The compound decomposes without melting.

Found %: N 7.91. $C_{25}H_{14}O_2N_2$. Calculated %: N 7.44.

When a large excess of hydroxylamine hydrochloride was used, and the same treatment as above, we obtained a substance that consisted mostly of the dioxime. It decomposes at 297-298° without melting.

Found %: N 10.10. $C_{25}H_{15}O_2N_3$. Calculated %: N 10.74.

Acetate of the Monoxime. The monoxime was dissolved in acetic anhydride and heated on the water bath for 1 hour. The light-yellow acetate deposited on cooling, and was recrystallized from dioxane.

Found %: N 6.83. $C_{27}H_{16}O_3N_2$. Calculated %: N 6.70.

Reduction of 4-Phenyl-2,3,6,5-dibenzoylenepyridine. A mixture of 1.2 g of the phenyldibenzoylenepyridine, 20 ml of glacial acetic acid and excess zinc dust was boiled for 3 hours. The liquid decolorized, and a violet fluorescence appeared. The hot solution was filtered and diluted with water. The white precipitate (X) was recrystallized from either acetone or alcohol. Yield 0.7 g, m. p. 303-305°.

Found %: N 3.53. $C_{25}H_{17}O_2N$. Calculated %: N 3.83.

Bis-Phenylisocyanate. The obtained reduction product (X) was heated with excess phenyl isocyanate and the obtained white crystals were washed with benzene.

Found %: N 7.24. $C_{39}H_{27}O_4N_3$. Calculated %: N 7.43.

SUMMARY

The reaction of benzalindandione with ammonium acetate in glacial acetic acid gave 4-phenyl-2,3,6,5-dibenzoylenepyridine. In a similar manner m-nitrobenzalindandione gave 4-(m-nitrophenyl)-2,3,6,5-dibenzoylenepyridine. The mechanism of this reaction was determined, from which it follows that from the easily obtained arylideneindandiones by simple reaction with ammonium acetate it is possible to go to complex polycyclic pyridines.

LITERATURE CITED

[1] G. Vanag and E. Vanag, Bull. Acad. Sci. Latvian SSR, 9 (86), 137 (1954).

[2] G. Ya. Vanag, Ya. F. Freimanis and G. F. Zakis, J. Gen. Chem. 27, 2509 (1957).*

[3] G. Ya. Vanag and G. Ya. Dubur, J. Gen. Chem. 27, 2729 (1957).*

[4] W. Wislicenus, A. Kötzle, Lieb. Ann. 252, 72 (1889).

[5] M. Ionescu, Bull. Soc. Chim., (4), 47, 210 (1930).

[6] G. Ya. Vanag and L. S. Geita, J. Gen. Chem. 26, 511 (1956).*

[7] G. Errera, Gazz. 32, II, 330 (1902).

[8] G. Errera, Gazz. 33, I, 417 (1903).

Received October 12, 1956

Latvian State University

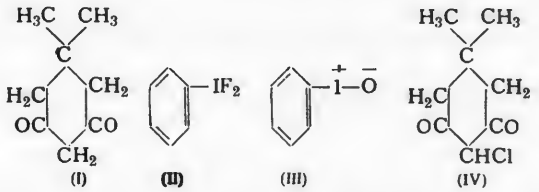
* Original Russian pagination. See C. B. Translation.

IODONIUM DERIVATIVES OF β-DIKETONES

1. REACTIONS OF DIMEDON WITH IODOSOBENZENE

E. Gudrinietse, O. Neiland and G. Vanag

Continuing our investigations [1, 2] of dimedon or 5,5-dimethyl-1,3-cyclohexanedions (I) derivatives, we undertook the task of preparing 2-fluorodimedon. Apparently, compounds containing fluorine in the active methylene group of β-diketones have in general been unknown up to now. To achieve the desired goal we tried the method of fluorinating with "bound" fluorine, and specifically, with aryl iododifluorides [3, 4]. Actually, a new compound was obtained when phenyl iododifluoride [2] was reacted with dimedon, but it did not contain fluorine. It proved that the same compound is obtained when dimedon is reacted with iodosobenzene (III). The new compound contains iodine, as well as the dimedon radical.



(I) (II) (III) (IV)

The reaction of iodosobenzene with dimedon proceeds smoothly in either chloroform, benzene or acetone solution. The obtained white felt-like substance with m. p. 130-132° (decomp.) was obtained from one molecule of dimedon and one molecule of iodosobenzene with cleavage of a molecule of water. The new substance is quite insoluble in water (up to 1%); however, it readily adds a molecule of water, forming the hydrate. The same hydrate is also formed in a water suspension of iodosobenzene and dimedon or its sodium salt. The substance holds water tenaciously, in which connection the melting point is lowered substantially. The substance decomposes in sunlight with the liberation of iodobenzene. The same decomposition also takes place when the substance is boiled with acids; it is stable to alkalies.

The substance shows some basic properties and forms addition products with hydrogen chloride and nitric acid. These adducts decompose above 80-90°; they rapidly hydrolyze with water. Thermal decomposition of the hydrogen chloride adduct and also boiling the original product with hydrochloric acid yields iodobenzene and 2-chlorodimedon (IV).

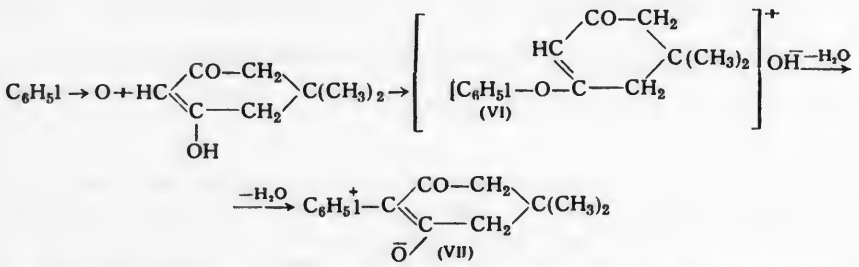
It is known that iodosobenzene (III) shows basic properties and is capable of forming salts with acids [3, 5], which decompose when treated with alkalies to iodosobenzene.

$$C_6H_5I \rightarrow O \xrightarrow{+HX} [C_6H_5IX]^{+}\overline{O}H \xrightarrow{+HX} \underset{(V)}{[C_6H_5IX]^{+}\overline{X}}$$

(X = Cl, F, CH_3COO, etc.).

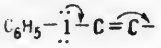
In the presence of concentrated sulfuric acid, iodosobenzene reacts with aromatic hydrocarbons to give diaryliodonium salts [6].

Dimedon also exists in solution as the enolic form [8, 20, 21]; consequently, it shows acid properties and can react with iodosobenzene by the general scheme to give the saltlike addition product (VI). Since the final product is formed with the cleavage of a molecule of water and is not cleaved by alkalies, then it is natural to assume that product (VI) will undergo further transformations. The most probable appears to be migration of the iodoaryl group from oxygen to carbon with the simultaneous cleavage of water and the formation of an inner salt (VIII) of the enolic form of dimedon and the iodonium compound.



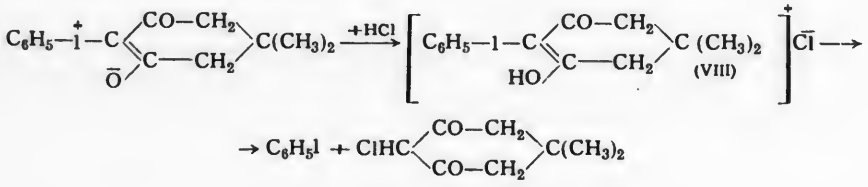
This new class of iodonium compounds can be given the name of iodones, due to some analogy between internal esters – lactones and the obtained compound (VII) – phenyldimedonyliodone.

Phenyldimedonyliodone is a dual compound. On the one hand it is a typical iodonium derivative, where the β-diketonic group figures as one of the radicals. Several references to aryl-alkyliodonium compounds exist in the literature [9-18]. Apparently, the most stable members are those containing an unsaturated radical. Evidently, conjugation of the unshared electron pair of iodine with the double bond occurs here.



The relative stability shown by phenyldimedonyliodone supports the premise that it is the enolic form of dimedon that participates in its structure.

On the other hand phenyldimedonyliodone is an inner salt. At elevated temperature under the influence of acid it is completely possible to cleave the bonds of the inner salt, followed by the usual decomposition of a typical iodonium compound. The formed adduct (VIII), similar to diaryliodonium salts [7, 19], decomposes at elevated temperature.



EXPERIMENTAL

Phenyldimedonyliodone (VII). a) A solution of 3.8 g of phenyl iododifluoride in 15 ml of chloroform was added to a solution of 1.5 g of dimedon in 10 ml of chloroform. The solution was allowed to evaporate, and the solid residue was washed with alkali and then with ether. Yield of crude phenyldimedonyliodone 2.9 (79%). M. p. 132-133° (decomp.)

b) Eleven grams of iodosobenzene was gradually added with vigorous stirring to a solution of 7 g of dimedon in 30 ml of chloroform. The reaction mixture warmed up, and the iodosobenzene dissolved. At the end of reaction the mixture was heated to the boil and then rapidly filtered into a porcelain dish. After evaporation of most of the chloroform, the thick felt-like mass was treated with 100 ml of ether. The yield of phenyldimedonyliodone was 12.5 g (73%), m. p. 130-132° (decomp.) If carefully dried starting substances and chloroform are

used, then when distilling off the solvent a cloudy liquid always flows back. The presence of water in this liquid, obtained by cleavage during reaction, was shown by the use of either anhydrous copper sulfate or calcium carbide.

c) A solution of 5.6 g of dimedon in 40 ml of acetone was treated with 8.8 g of iodosobenzene, the mixture boiled 15 minutes, 30 ml of acetone distilled off, and the residue treated with 40 ml of 5% potassium hydroxide solution. The residue was washed with ether. The yield of phenyldimedonyliodone 8.7 g (63%), m. p. 126-128° (decomp.) Recrystallization from anhydrous alcohol gave the compound as white long slender needles, m. p. 139° (decomp.) Yield 4.3 g (50%).

d) A mixture of 1.4 g of finely divided dimedon, 2.2 g of iodosobenzene and 20 ml of water was stirred for 1 hour. The filtered precipitate was washed with ether. The yield of phenyldimedonyliodone hydrate was 2.37 g (66%), m. p. 90-94°.

e) A mixture of 2.8 g of dimedon, 0.8 g of sodium hydroxide, 4.4 g of iodosobenzene and 30 ml of water was stirred for 48 hours (with standing overnight). The obtained crystals were washed with water and ether. Yield of phenyldimedonyliodone hydrate 6 g (83%), m. p. 126° (decomp.) Recrystallization from alcohol with the addition of ether gave the phenyldimedonyliodone hydrate as large prismatic crystals. Yield 4 g (66%), m. p. 126-127° (decomp.)

Found %: I 34.94, 34.71. $C_{14}H_{17}O_3I$. Calculated %: I 35.28.

The substance was dried in vacuo over phosphorus pentoxide (7 days). The dehydrated substance melts at 138°.

Found %: H_2O 5.06. $C_{14}H_{15}O_2I \cdot H_2O$. Calculated %: H_2O 5.00.
Found %: I 36.55, 37.09. $C_{14}H_{15}O_2I$. Calculated %: I 37.13.

Phenyldimedonyliodone is readily soluble in chloroform and glacial acetic acid, soluble in alcohol, benzene and acetone, and insoluble in ether and benzine. Its solutions have a yellow color and a very bitter taste.

Phenyldimedonyliodone Adducts. a) With Hydrogen Chloride. A solution of 0.684 g of phenyldimedonyliodone in 10 ml of chloroform was treated at 0° with an excess of hydrogen chloride in ether solution. The obtained white finely crystalline precipitate was washed with ether. Yield of the adduct (VIII) 0.637 g (88%), m. p. 72-73° (decomp.) After recrystallization from alcohol with the addition of ether, m. p. 80° (decomp.) Complete hydrolysis occurs when it is dissolved in water.

Found %: HCl (titration) 9.09, 9.20. $C_{14}H_{15}O_2I \cdot HCl$. Calculated %: HCl 9.64.

The obtained adduct (0.57 g) was heated at 90-110° for 3 hours. We obtained 0.22 g (80%) of the chlorodimedon (IV) with m. p. 159° (from the literature: 161°). Its mixed melting point with the pure chlorodimedon is not depressed.

b) With Nitric Acid. A solution of 0.34 g of phenyldimedonyliodone in 3 ml of absolute ether was treated with 20 ml of absolute ether and several drops of fuming nitric acid. An emulsion was obtained, which soon crystallized. The crystals were washed with ether. Yield of the adduct 0.25 g (62%), m. p. 89° (decomp.) Recrystallization from alcohol with the addition of benzine gave handsome white leaflets with m. p. 89° (decomp.)

Found %: HNO_3 15.45; N 3.45. $C_{14}H_{15}O_2I \cdot HNO_3$. Calculated %: HNO_3 15.30; N 3.46.

The obtained adduct is soluble in alcohol and acetone, and insoluble in ether; it dissolves in water easily, but immediately suffers hydrolysis with the separation of the phenyldimedonyliodone hydrate.

Cleavage of Phenyldimedonyliodone With Hydrochloric Acid. A mixture of 3.42 g of phenyldimedonyliodone, 30 ml of water and 5 ml of concentrated hydrochloric acid was boiled in a flask under reflux. The water and iodobenzene were distilled off. The residue in the flask crystallized to give the chlorodimedon (IV). Yield 1.2 g (70%), m. p. 160° (literature: 161°). The mixed melting point with pure chlorodimedon is not depressed.

SUMMARY

Dimedon reacts very easily with iodosobenzene, forming a new type of iodonium compound – phenyldimedonyliodone.

Phenyldimedonyliodone shows some basic properties and forms addition products with hydrochloric and nitric acids.

Phenyldimedonyliodone is quite stable to alkalies. When treated with hydrochloric acid it shows the characteristic cleavage of iodonium compounds with the liberation of iodobenzene and the formation of chlorodimedon.

LITERATURE CITED

[1] E. Gudrinietse, O. Nieland and G. Vanag, J. Gen. Chem. 24, 1863 (1954).*

[2] O. Ya. Neiland, E. Yu. Gudrinietse and G. Ya. Vanag, J. Gen. Chem. 26, 3139 (1956).*

[3] W. Bockemüller, Ber. 64, 522 (1931).

[4] B. S. Garvey, L. F. Halley, C. F. H. Allen, J. Am. Chem. Soc. 59, 1827 (1937).

[5] C. Willgerodt, Ber. 25, 3498 (1892).

[6] F. Beringer, M. Drexler, E. M. Gindler and Ch. C. Lumpkin, J. Am. Chem. Soc. 75, 2705 (1953).

[7] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and Ch. C. Lumpkin, J. Am. Chem. Soc. 75, 2708 (1953).

[8] F. Arndt, L. Loewe, R. Ginkök, Ch. A. 41, 3761 (1947).

[9] E. M. Brainina and R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 623.

[10] J. Thiele, A. Umnoff, Lieb. Ann. 369, 147 (1909).

[11] C. Willgerodt, Ber. 28, 2110 (1895).

[12] C. Willgerodt, V. A. Howells, Ber. 33, 850 (1900).

[13] C. Willgerodt, E. Rampacher, Ber. 34, 3676 (1901).

[14] C. Willgerodt, K. Dammann, Ber. 34, 3687 (1901).

[15] C. Willgerodt, A. Desaga, Ber. 37, 1309 (1904).

[16] C. Willgerodt, L. Brandt, J. pr. Ch. 69, 446 (1904).

[17] C. Willgerodt, J. pr. Ch. 71, 551 (1905).

[18] C. Willgerodt, T. Umbach, Lieb. Ann. 327, 284 (1897).

[19] E. Lewis, Ch. Stout, J. Am. Chem. Soc. 76, 4619 (1954).

[20] E. R. Blout, V. W. Eager, D. C. Silverman, J. Am. Chem. Soc. 68, 566 (1946).

[21] M. I. Kabachnik, Proc. Acad. Sci. USSR 83, 859 (1952).

Received August 11, 1956

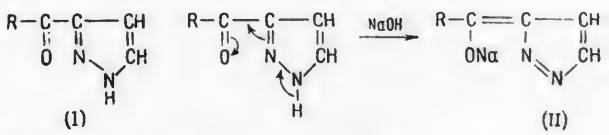
Latvian State University

* Original Russian pagination. See C. B. Translation.

SPECTROSCOPIC STUDY OF 3-ACYLPYRAZOLES

N. K. Kochetkov and Ivan Ambrush

A new method was recently developed [1] in our laboratory for the preparation of 3-pyrazolyl ketones of general formula (I), and it was unexpectedly discovered that these compounds are soluble in caustic alkalies. It was postulated that salt formation takes place here in accordance with the scheme



(I) (II)

with disturbance of the aromatic structure of the pyrazole ring.

A more detailed study of the behavior of 3-acylpyrazoles and of their dual reactivity was begun by us. The first results of this study are presented here.

To confirm the above mentioned postulation, we first studied the ultraviolet absorption spectra of some 3-acylpyrazoles in water solutions as a function of the pH of the medium. Conversion of (I) into (II) should cause such profound changes in the electron structure with a redistribution of the double bonds that this phenomenon, without doubt, should be reflected in substantial manner on the UV-absorption spectra of these compounds. At the same time from the data for the UV-absorption spectra of ketones of the pyrazole series in media of different pH it is possible to calculate their acidity constant; the utilization of other methods for this purpose is made difficult due to the poor solubility of the mentioned compounds. The acidity constants of 3-acylpyrazoles are of interest in interpreting their chemical properties, since at the present time the studies of M. I. Kabachnik [2] have established that a close relationship exists between tautomerism and acid-base equilibrium.

Our investigations were run on the example of three 3-pyrazolyl ketones: methyl-3-pyrazolyl ketone, tert-butyl-3-pyrazolyl ketone and phenyl-3-pyrazolyl ketone. Solutions of these compounds in water or in 1 N alkali obey the Lambert-Beer law in the limits of the concentrations used. The spectra of these compounds in media of various pH are shown in Figs. 1, 2 and 3.

In neutral or close to neutral solutions the spectra consist of two bands – an intense band in the short-wave region with a well defined maximum (235, 238 and 260 mμ, respectively) and a weak band in the long-wave region, which was detected only as two inflection points. As the alkalinity of the medium is increased the intensity of the long-wave bands increases, and the inflection points disappear. In strongly alkaline solutions (pH 13-14) a well-defined maximum appears in the long-wave region (270, 270 and 288 mμ, respectively), the short-wave band disappears completely in the case of the methyl and tert-butyl ketones, while in the case of the phenyl-3-pyrazolyl ketone it remains as a horizontal section on the spectral curve. Attention is attracted to the fact that the spectra of methyl-3-pyrazolyl ketone and tert-butyl-3-pyrazolyl ketone are very similar. From this it can be concluded that an alkyl group linked to the carbonyl in 3-acylpyrazoles exerts but slight influence on the spectrum, and that the character of the latter is determined entirely by the pyrazole ring and the carbonyl group connected to it in the 3 position.

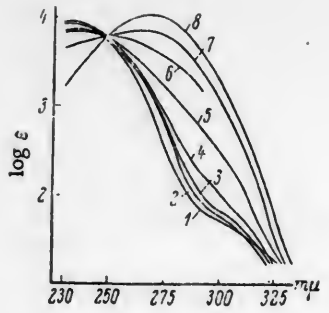


Fig. 1. Ultraviolet absorption spectra of methyl-3-pyrazolyl ketone in media of various pH.
1) in 1 N HCl; 2) pH 7; 3) pH 9; 4) pH 10; 5) pH 11; 6) pH 11.5; 7) pH 12; 8) pH 13-14.

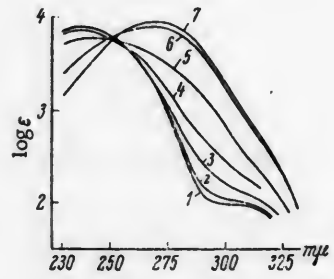


Fig. 2. Ultraviolet absorption spectra of tert-butyl-3-pyrazolyl ketone in media of various pH.
1) pH 8; 2) pH 10; 3) pH 11; 4) pH 11.5; 5) pH 12; 6) pH 13; 7) pH 14.

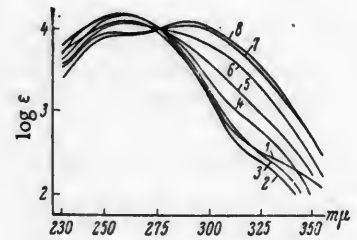
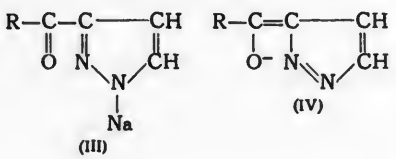


Fig. 3. Ultraviolet absorption spectra of phenyl-3-pyrazolyl ketone in media of various pH.
1) in 1 N HCl; 2) pH 7; 3) pH 10; 4) pH 11; 5) pH 11.5; 6) pH 12; 7) pH 13; 8) pH 14.

It is characteristic that the spectral curves of 3-acylpyrazoles in solutions of various pH have an isosbestic point (general point of intersection for all of the curves of a given substance), the existence of which is evidence that equilibrium is present in these solutions. Also, in support of the presence of reversible equilibrium in solutions of 3-acylpyrazoles is the fact that acid solutions of a given ketone, obtained either by direct solution or by acidification of an alkaline solution, all have exactly the same spectrum. The spectra for methyl-3-pyrazolyl ketone and phenyl 3-pyrazolyl ketone were also taken in strongly acid medium; the obtained curves are essentially the same as the spectra of these compounds in neutral medium.

The results obtained in the spectroscopic study lead us to the following conclusion: 3-acylpyrazoles are weak acids, in contrast to pyrazole itself and 3-alkylpyrazoles, which, as is known, possess weakly basic properties (the basicity constant of pyrazole is 3.0×10^{-12}, and that of 3-methylpyrazole is 3.6×10^{-11} [3]). Examination of the obtained spectra does not indicate the presence of basic properties for 3-acylpyrazoles. A sharp change in the absorption maximum of 3-acylpyrazoles in aqueous alkaline solutions is evidence that substantial redistribution of the double bonds in the molecule occurs under the influence of alkali. In other words, metal derivatives of 3-acylpyrazoles have a different structure from that of the neutral 3-acylpyrazole molecule. More exactly, since the spectra of 3-acylpyrazoles in media of various pH indicate the presence of acidic dissociation for these compounds, the mentioned difference should be attributed essentially to the corresponding anion. In view of the fact that tert-butyl-3-pyrazolyl ketone and phenyl-3-pyrazolyl ketone also suffer similar transformation, the formation of the metal derivative due to enolization of the carbonyl group in the direction of the alkyl radical is excluded. The formation of a salt having structure (III) is highly improbable, since the anion of a salt



of this type can rearrange into an ion of type (IV) due to the greater electronegativity of oxygen when compared to nitrogen. Consequently structure (II), which we proposed [1] for the metal derivatives of 3-acylpyrazoles, seems most probable. Attention is attracted to the fact that the spectra of 3-acylpyrazoles in alkaline medium suffer bathochromic shift. This can be due to disturbance of the aromatic structure of the pyrazole ring. As is well known, a similar shift of the spectrum occurs in the transition from an aromatic to a quinoid structure. In the anion of salt (II) the pyrazole ring has assumed, as it were, a "quinoid" structure, and the shift of the absorption maximum observed by us is in agreement with this conclusion.

As was indicated above, determining the acidity constants of 3-acylpyrazoles was of considerable interest. For this we utilized the calculation method proposed by Stenström and Goldsmith [4]

$$K = a_H \frac{C_{A^-}}{C_{AH}} a_H \frac{\varepsilon - \varepsilon_{AH}}{\varepsilon_{A^-} - \varepsilon}$$

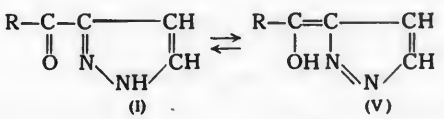
where K is the acidity constant of the 3-acylpyrazole, a_H is the activity of the proton, C_A is the concentration of the 3-acylpyrazole anion in solution, C_{AH} is the concentration of undissociated 3-acylpyrazole in solution, ϵ is the molecular coefficient of absorption at a given pH, ϵ_{AH} is the molecular absorption coefficient of the undissociated 3-acylpyrazole, and ϵ_{A^-} is the molecular absorption coefficient of the anion.

We took pH = $-\log a_H$ (cf. [5]), which is permissible at a low ionic strength for the solutions used, and we also took $\epsilon_{A^-} = \epsilon$ at pH 14. The last assumption is based on the fact that the values of ϵ at pH 13 and 14 are close, and also, that the values of K calculated for different wavelengths and pH show good agreement, and, finally, on the fact that the values of ϵ_{A^-}, calculated by another method (see below), are close to the values of ϵ at pH 14. ϵ_{AH} was calculated directly from experimental data, since in the pH interval 6-8 the spectral curves coincide within the limits of experimental error and consequently correspond to the spectrum of the undissociated pyrazolyl ketone; as ϵ_{AH} we took the average value of two or three determinations at different pH. The acidity constants were calculated from the curves obtained at pH 11, 11.5 and 12 (and at pH 13 for phenyl-3-pyrazolyl ketone) and in that wavelength region in which the spectral curves at different pH are furthest removed from each other, in order to reduce the calculation error. The following values for the acidity constant were obtained: for methyl 3-pyrazolyl ketone, $K = (1.42 \pm 0.03) \cdot 10^{-12}$; pK = 11.85 ; for tert-butyl-3-pyrazolyl ketone, $K = (3.74 \pm 0.06) \cdot 10^{-13}$; pK = 12.42; for phenyl-3-pyrazolyl ketone, $K = (1.07 \pm 0.01) \cdot 10^{-12}$; pK = 11.97.

For verification, the calculations were repeated with the assumption that not only K, but also ϵ_{A^-} are unknown; their values were calculated by the method of least squares from the spectral data at different pH [6]. The values of K calculated in this manner lie close to the presented data; however, we adopted the latter, since the second method is the less accurate in the given case.

The values of the acidity constants of the investigated ketones lie close to each other. From these data it can be postulated as a preliminary conclusion that the anion of methyl-3-pyrazolyl ketone is stabilized when compared with the anion of tert-butyl-3-pyrazolyl ketone by the σ,π-conjugation effect (between the C—H bond of the methyl group and the C=C bond).

The existence of acidic dissociation for 3-acylpyrazoles of form (I) with the formation of anions (IV) makes possible the presence of tautomeric equilibrium between forms (I) and (V)



(I) (V)

In such a case our measured acidity constants are actually the ionization constants of equilibrium mixtures (I) and (V). However, it is impossible from the existing data to arrive at a conclusion as to the position of equilibrium in such systems.

We consider it our pleasant task to thank Academy Member A. N. Nesmeyanov for his valuable guidance, and also L. A. Kazitsyna for his advice and assistance.

EXPERIMENTAL

Starting Substances. Methyl-3-pyrazolyl ketone and phenyl-3-pyrazolyl ketone were obtained by the earlier described method [1, 7] from the corresponding β-chlorovinyl ketones and diazomethane. Tert-butyl-3-pyrazolyl ketone was obtained by the same method; it is a colorless crystalline powder with m. p. 99-100°.

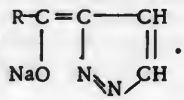
Found %: C 63.13, 63.05; H 7.89, 7.94. $C_8H_{12}ON_2$. Calculated %: C 63.13; H 7.95.

Solutions. As solvents we used standard buffer solutions: phosphate buffers (KH_2PO_4 + NaOH) in the pH range from 6 to 8, and glycine solutions in the pH region from 9 to 13. As a solution with pH 14 we used 1 N sodium hydroxide solution. The sample of investigated substance was weighed on a microbalance and was dissolved in the calculated volume of solvent. The desired solution concentrations (in moles per liter of solvent) were prepared by dilution of the primary solution.

Spectra. An SF-4 spectrophotometer was used to measure the optical density of the solutions. Each measurement was repeated, in which connection a difference of up to 1-1.5% was permitted in the obtained optical density values. A hydrogen lamp served as the light source. The solution was placed in a quartz cuvette with an area 1 cm square. To verify the Lambert-Beer law we also used round cuvettes with quartz apertures and a quartz insert, attached to the apparatus. The Lambert-Beer law was verified for the case of methyl-3-pyrazolyl ketone at λ 235 mμ in water solution in the concentration range 3.70×10^{-5}-6.57×10^{-3} mole/liter of solvent and in 1 N caustic solution in the concentration range 3.94×10^{-5}-6.70×10^{-3} mole/liter of solvent. For tert-butyl-3-pyrazolyl ketone and phenyl-3-pyrazolyl ketone the concentration limits in moles per liter of solvent, for which compliance with the Lambert-Beer law was verified at 270 mμ for the first and at 260 mμ for the second, were respectively: in water $3.78 \cdot 10^{-5}$-$1.51 \cdot 10^{-3}$ and $3.04 \cdot 10^{-5}$-$2.02 \cdot 10^{-3}$, and in 1 N caustic solution 4.04×10^{-5}-1.55×10^{-3}. All of the solutions used had concentrations that did not go beyond these limits.

The obtained spectral curves are shown in Figs. 1, 2 and 3. From the spectral data we calculated the acidity constants by the method described in the general part of the paper.

SUMMARY

1. The ultraviolet absorption spectra of 3-acylpyrazoles in water solutions at various pH values were studied. The obtained results support the postulation that the metal derivatives of 3-acylpyrazoles have the structure  .

2. It was shown that 3-acylpyrazoles are weak acids, and their acidity constants were calculated from the spectroscopic data.

LITERATURE CITED

[1] A. N. Nesmeyanov and N. K. Kochetkov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 686.

[2] M. I. Kabachnik, Proc. Acad. Sci. USSR 83, 407, 859 (1952).

[3] G. Dedichen, Ber. 39, 1831 (1906).

[4] W. Stenström, N. Goldsmith, J. Phys. Chem. 30, 1683 (1926).

[5] A. I. Shatenshtein, Theory of Acids and Bases (Moscow-Leningrad, 1949), 91.*

[6] L. A. Flexser, L. P. Hammett, A. Dingwall, J. Am. Chem. Soc. 57, 2103 (1935).

[7] A. N. Nesmeyanov and N. K. Kochetkov, Proc. Acad. Sci. USSR 77, 65 (1951).

Received October 1, 1956

Moscow State University

*In Russian.

SYNTHESIS OF ARYL β-ACYLVINYL SULFONES AND ARYL β-ACYLVINYL SULFOXIDES

N. K. Kochetkov and V. N. Vinogradova

β-Acylvinyl sulfones $RCOCH=CHSO_2Ar$ and β-acylvinyl sulfoxides $RCOCH=CHSOAr$ present definite interest, both from the viewpoint of utilizing them for the synthesis of some inaccessible sulfur compounds and in order to solve the problem of the mutual influence exerted by the carbonyl group and the SO_2 and SO groups on the adjacent double bond. However, compounds of this type are practically unknown. Thus, sulfoxides of this type have not been obtained, while of the sulfones only phenyl-β-benzoylvinyl sulfone is known, synthesized from the corresponding saturated compound by the technique of first bromination and then dehydrobromination [1].

In the present paper we give some data on a new general method for the synthesis of these compounds, based on the oxidation of the corresponding β-acylvinyl sulfides $RCOCH=CH-S-Ar$. The latter in turn are easily obtained by the ketovinylation of thiophenols and are described by us in a previous paper [2]. All of the β-acylvinyl sulfides $RCOCH=CH-S-Ar$ needed for this study were prepared specifically by this method. In addition to the members described in the previous communication [2], we synthesized two new sulfides: phenyl β-isovaleroylvinyl sulfide and p-tolyl-β-isovaleroylvinyl sulfide. These compounds, being high-boiling liquids, have a high exaltation of the molecular refraction. The exaltation value of the sulfides exceeds the exaltation of the β-phenoxyvinyl ketones $RCOCH=CHOAr$ [3] and is less than the exaltation of the β-amino-vinyl ketones $RCOCH=CHNR_2$ [4, 5]. This again confirms the earlier expressed [2, 6] postulation that the reactivity of a carbonyl group with the heteroatom of a β-substituted vinyl ketone decreases in the order: $RCOCH=CH-NR_2$ > $RCOCH=CH-S-Ar$ > $RCOCH=CHOAr$ > $RCOCH=CH-Cl$, which is associated with a reduction in the ability of the corresponding heteroatom to share its free electron pair.

The oxidation of aryl-β-acylvinyl sulfides to aryl-β-acylvinyl sulfones can be accomplished provided a mild specific oxidizing agent is used, not attacking the quite labile acylvinyl group. We chose hydrogen peroxide as such an oxidizing agent, widely used for the oxidation of sulfides, including unsaturated sulfides [7]. The oxidation is run by reacting the aryl-β-acylvinyl sulfides with excess hydrogen peroxide in acetic acid in the presence of a drop of sulfuric acid at room temperature, and smoothly gives pure aryl-β-acylvinyl sulfones:

$$RCOCH=CH-S-Ar \xrightarrow{H_2O_2} RCOCH=CHSO_2Ar$$

The yields of the alkyl derivatives ($R=CH_3$, C_3H_7, iso-C_4H_9) constitute 30-50%; phenyl-β-benzoylvinyl ketone ($R=C_6H_5$) was obtained in almost quantitative yield.

It should be mentioned that when an equimolar amount of hydrogen peroxide is used the oxidation does not go to completion and the isolation of a pure sulfone is made extremely difficult. For these reasons the reaction requires a relatively long time (3-4 days).

The obtained aryl-β-acylvinyl sulfones are stable solids that crystallize well. In order to confirm their structure we synthesized the compounds by a different method. It proved that the aryl-β-acylvinyl sulfones are obtained smoothly also by the direct ketovinylation of arylsulfinic acids by the scheme

$$RCOCH=CHCl + NaSO_2Ar \longrightarrow RCOCH=CHSO_2Ar + NaCl$$
$$(R=CH_3,\ C_6H_5)$$

The reaction proceeds smoothly if the β-chlorovinyl ketone is reacted with the sodium salt of the arylsulfinic acid in water solution, and the aryl-β-acylvinyl ketones are obtained in 40-50% yield. This reaction, besides conclusively proving the structure of the compounds obtained by the oxidation of aryl-β-acylvinyl sulfides, can also serve as a very convenient method for the synthesis of aryl-β-acylvinyl sulfones, in a number of cases being in no way inferior to the first method described here. It is a new example of the ketovinylation reaction [8] and once again emphasizes the quite general character of this new reaction. It is interesting to mention that attempts to accomplish the ketovinylation of carboxylic acids, formal analogs of sulfinic acids, repeatedly undertaken in our laboratory, have up to now been unsuccessful.

In the oxidation of aryl-β-acylvinyl sulfides to the sulfones there obviously exists an intermediate stage where the corresponding sulfoxides are formed, evidence of which is the fact that a mixture of compounds is obtained when the oxidation is run with an equimolar amount of hydrogen peroxide. In connection with this we made an attempt to find the conditions for the oxidation of aryl-β-acylvinyl sulfides to the sulfoxides. Actually, by running the oxidation with an exactly equivalent amount of hydrogen peroxide at 0° we were able to hold the oxidation to the sulfoxide stage.

$$RCOCH{=}CH{-}S{-}Ar \xrightarrow{H_2O_2} RCOCH{=}CHSOAr$$

The reaction proceeds quite smoothly under the indicated conditions, and the aryl β-acylvinyl sulfoxides are isolated without difficulty from the reaction mixture. Here, a certain amount of the original sulfide always remains unchanged; however, the isolation of the pure sulfoxide does not present any difficulties. It should be kept in mind that both the use of excess oxidizing agent and changing the reaction temperature to room temperature lead to the appearance of substantial amounts of sulfone in the reaction mixture, and in such case the isolation of the pure sulfoxide is now made difficult.

The obtained sulfoxides, the same as the sulfones, are stable solids that crystallize well. Their melting points are somewhat above the melting points of the corresponding sulfones. The structure of the obtained compounds as being sulfoxides was confirmed by us by the oxidation of one of their members – phenyl-β-benzoylvinyl sulfoxide – to the corresponding sulfone.

$$C_6H_5COCH{=}CHSOC_6H_5 \xrightarrow{H_2O_2} C_6H_5COCH{=}CHSO_2C_6H_5$$

This reaction, understandably not possessing preparative interest, was run under the conditions used in the direct oxidation of acylvinyl sulfides to sulfones, i.e., by the action of excess hydrogen peroxide at room temperature.

EXPERIMENTAL

Phenyl-β-isovaleroylvinyl Sulfide. Obtained by the earlier described method [2] from 15.5 ml (16.2 g) of thiophenol and 18 g of isobutyl-β-chlorovinyl ketone. Yield 22 g (83%).

B. p. 149-151° (4 mm), n_D^{20} 1.5837, d_4^{20} 1.0610, MR_D 69.44; calc. 66.15; EMR_D + 3.29.

Found %: C 70.75, 70.74; H 7.33, 7.46. $C_{13}H_{16}OS$. Calculated %: C 70.86; H 7.32.

Phenyl-β-isovaleroylvinyl sulfide is a yellow liquid, gradually darkening on storage, and soluble in ether, chloroform, acetone and glacial acetic acid.

p-Tolyl-β-isovaleroylvinyl Sulfide. Obtained by the earlier described method from 8 g (0.05 mole) of isobutyl β-chlorovinyl ketone and 7 g (0.06 mole) of thiocresol. Yield 5.7 g (60%).

B. p. 154-156° (2 mm), n_D^{20} 1.5759, d_4^{20} 1.0310, MR_D 75.19; calc. 70.79; EMR_D + 4.40.

Found %: C 72.26, 72.18; H 7.69, 7.78. $C_{14}H_{18}OS$. Calculated %: C 71.73; H 7.74.

Phenyl-β-acetylvinyl Sulfone. 1) A solution of 1 g of phenyl-β-acetylvinyl sulfide (0.0056 mole) in 2.4 ml of glacial acetic acid was treated with 3.3 ml of 30% perhydrol (0.032 mole) containing 1 drop of concentrated sulfuric acid. The reaction mixture was let stand 4 days, after which ice water was added until the cloudiness was permanent. The separated oil was extracted with ether and dried over fused magnesium sulfate. The

oil remaining after evaporation of the ether, crystallized. Recrystallization from petroleum ether gave 0.35 g (30%) of substance, m. p. 61-62°.

Found %: C 57.31, 57.40; H 4.97, 5.11. $C_{10}H_{10}O_3S$. Calculated %: C 57.14; H 4.79.

Phenyl-β-acetylvinyl sulfone was obtained as colorless needles, soluble in ether, benzene and glacial acetic acid.

2) To a solution of 2 g (0.01 mole) of the sodium salt of benzenesulfinic acid in 10 ml of water was added with constant stirring 1 g (0.01 mole) of methyl-β-chlorovinyl ketone in drops. Stirring was continued for 6 hours. The obtained precipitate was filtered and dried in the air. Yield 0.8 g (39.5%), m. p. 61-62° (from petroleum ether). Its mixed melting point with the substance obtained by the first method was not depressed.

Phenyl-β-butyroylvinyl Sulfone. Obtained by the treatment of 1 g (0.005 mole) of phenyl-β-butyroylvinyl sulfide in 2 ml of glacial acetic acid with a mixture of 1.2 ml of 30% perhydrol (0.035 mole), 3 ml of glacial acetic acid and 1 drop of concentrated sulfuric acid. Yield 0.5 g (43%), m. p. 64-65° (from alcohol).

Found %: C 60.92, 60.73; H 6.26, 6.23. $C_{12}H_{14}O_3S$. Calculated %: C 60.46; H 5.92.

Phenyl β-butyroylvinyl sulfone is a white crystalline substance, soluble in ether, benzene and glacial acetic acid.

Phenyl-β-isovaleroylvinyl Sulfone. Obtained from 4 g (0.018 mole) of phenyl-β-isovaleroylvinyl sulfide in 10 ml of glacial acetic acid by treatment with a mixture of 4 ml of concentrated sulfuric acid. The addition of ice gave a yellow flocculent precipitate which was filtered and dried in a desiccator over phosphorus pentoxide. Yield 2.2 g (46%), m. p. 82-84° (from methanol).

Found %: C 61.78, 61.84; H 6.49, 6.52. $C_{13}H_{16}O_3S$. Calculated %: C 61.87; H 6.39.

Phenyl-β-isovaleroylvinyl sulfone is a bright yellow crystalline substance, soluble in ether, benzene and glacial acetic acid.

p-Tolyl-β-isovaleroylvinyl Sulfone. Obtained from 3.5 g (0.015 mole) of p-tolyl-β-isovaleroylvinyl sulfide in 10 ml of glacial acetic acid by treatment with a mixture of 3.5 ml of 30% perhydrol, 5 ml of glacial acetic acid and 0.1 ml of concentrated sulfuric acid. Yield 2 g (49%), m. p. 86-87° (from methanol).

Found %: C 63.67, 63.68; H 7.01, 7.00. $C_{14}H_{18}O_3S$. Calculated %: C 63.10; H 6.81.

Phenyl-β-benzoylvinyl Sulfone. 1) Obtained from 1 g of phenyl-β-benzoylvinyl sulfide in 25 ml of glacial acetic acid by treatment with 3 ml of 30% perhydrol. After standing for 4 days a yellow crystalline precipitate deposited, which was filtered and dried in a desiccator over calcium chloride. The addition of ice to the mother liquor gave a little more of the precipitate. Yield 1.1 g (96%), m. p. 112-112.5° (from methyl alcohol). Literature [1]: m. p. 114°.

Phenyl-β-benzoylvinyl sulfone is a yellow crystalline substance, soluble in ether and benzene.

2) A solution of 3 g (0.015 mole) of the sodium salt of benzenesulfinic acid in 10 ml of water was treated with constant mechanical stirring with 2 g (0.012 mole) of phenyl-β-chlorovinyl ketone in drops. The stirring was continued for 6 hours. The obtained yellow crystalline precipitate was filtered and dried in a desiccator over calcium chloride. Yield 1.65 g (50%), m. p. 112-112.5° (from methanol). Its mixture with the substance obtained by method 1 did not give a melting point depression.

Found %: C 66.25, 66.37; H 4.73, 4.81. $C_{15}H_{12}O_3S$. Calculated %: C 66.13; H 4.44.

Phenyl-β-benzoylvinyl Sulfoxide. To a solution of 1 g (0.004 mole) of phenyl-β-benzoylvinyl sulfide in 1 ml of glacial acetic acid was added, with ice-water cooling, a mixture of 0.36 ml (0.004 mole) of 30% perhydrol, 2.1 ml of glacial acetic acid and 1 drop of concentrated sulfuric acid. The reaction mixture was let stand overnight at 0°. The addition of ice gave a flocculent precipitate, which was filtered and dried over calcium chloride. Yield 0.65 g (60.7%), m. p. 126-127.5° (from methanol).

Found %: C 70.33, 70.40; H 4.74, 4.76. $C_{15}H_{12}O_2S$. Calculated %: C 70.33; H 4.72.

Phenyl β-benzoylvinyl sulfoxide was obtained as slightly yellowish crystals, soluble in ether, benzene and glacial acetic acid.

Phenyl-β-acetylvinylsulfoxide. Obtained from 1 g (0.005 mole) of phenyl-β-acetylvinyl sulfide by treatment with a mixture of 1 ml (0.005 mole) of 30% perhydrol, 5 ml of glacial acetic acid and 1 drop of concentrated sulfuric acid. After addition of ice, the water solution was extracted 3 times with ether, dried over fused magnesium sulfate, the ether evaporated, and the residue recrystallized from petroleum ether. Yield 0.65 g (59.6%), m. p. 65-66° (from methanol).

Found %: C 61.37, 61.22; H 5.29, 5.20. $C_{10}H_{10}O_2S$. Calculated %: C 61.80; H 5.19.

Phenyl-β-acetylvinyl sulfoxide was obtained as colorless crystals, soluble in ether, benzene and glacial acetic acid.

Phenyl-β-isovaleroylvinyl Sulfoxide. Obtained from 2.2 g (0.01 mole) of phenyl-β-isovaleroylvinyl sulfide and 1 ml of 30% perhydrol in 5 ml of glacial acetic acid with 1 drop of concentrated sulfuric acid. Yield 0.55 g (23.3%), m. p. 96-97° (from petroleum ether).

Found %: C 66.28, 66.38; H 6.53, 6.42. $C_{15}H_{16}O_2S$. Calculated %: C 66.06; H 6.82.

Phenyl-β-isovaleroylvinyl sulfoxide was obtained as colorless needles, soluble in ether, benzene and glacial acetic acid.

Oxidation of Phenyl-β-benzoylvinyl Sulfoxide. To a solution of 0.1 g of phenyl-β-benzoylvinyl sulfoxide (0.0004 mole) in 5 ml of glacial acetic acid was added 1 ml of 30% perhydrol (0.009 mole). The reaction mixture was allowed to stand for 4 days. The addition of ice water gave a precipitate which was filtered, and dried in a desiccator over phosphorus pentoxide. Yield 0.08 g (75%), m. p. 111-112° (from methanol). The melting point was not depressed when the compound was mixed with the earlier obtained specimen of the sulfone.

SUMMARY

1. Two methods were developed for the synthesis of aryl-β-acylvinyl sulfones: a) oxidation of aryl-β-acylvinyl sulfides with excess hydrogen peroxide in glacial acetic acid, and b) ketovinylation of arylsulfinic acids in water medium.

2. A method was developed for the synthesis of aryl-β-acylvinyl sulfoxides by the oxidation of aryl-β-acylvinyl sulfides with an equimolecular amount of hydrogen peroxide in acetic acid at 0°.

LITERATURE CITED

[1] E. P. Kohler, R. G. Larsen, J. Am. Chem. Soc. 57, 1448 (1935).

[2] N. K. Kochetkov and V. N. Vinogradova, J. Gen. Chem. 27, 460 (1957).*

[3] N. K. Kochetkov, M. I. Rybinskaya and A. N. Nesmeyanov, Proc. Acad. Sci. USSR, 79, 799 (1951).

[4] N. K. Kochetkov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 991.*

[5] A. N. Nesmeyanov, N. K. Kochetkov and Ya. Dombrovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 179.*

[6] A. N. Nesmeyanov, N. K. Kochetkov, M. I. Rybinskaya and E. V. Uglova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 649.*

[7] E. P. Kohler, H. Potter, J. Am. Chem. Soc. 57, 1316 (1935).

[8] N. K. Kochetkov, Prog. Chem. 24, 32 (1955).

Received October 1, 1956

Moscow State University

* Original Russian pagination. See C. B. Translation.

ALLYLIC REARRANGEMENTS

XIX. REACTIONS OF ORGANOMAGNESIUM COMPOUNDS AND DIETHYL SODIUM PHOSPHITE WITH ISOMERIC ISOPRENE HYDROCHLORIDES AND METHOXYCHLOROISOHEXENES

A. N. Pudovik and I. V. Shergina

In studying the reactions of phenylmagnesium bromide with the isomeric methoxychloropentenes it was shown by us [1] that independent of the structure of the allylic halide isomer the mixtures of methoxyphenylpentenes formed have the same composition, containing 64-69% 1-methoxy-5-phenyl-3-pentene and 31-36% 1-methoxy-3-phenyl-4-pentene.

Taking into consideration the stability of methoxychloropentenes under the experimental conditions used, we came to the conclusion that these reactions proceed by an ionic mechanism. This conclusion is in agreement with the results obtained in previous studies by a number of authors [2-4], who studied the reactions of organomagnesium compounds with the isomeric butenyl and pentenyl chlorides and bromides. In similar experiments in which the isomeric ethoxychloropentenes and butoxychloropentenes were reacted with ethylmagnesium, butylmagnesium and phenylmagnesium bromides [5] we obtained in each case only a single unsaturated ether, in structure corresponding to the primary form of the chloride. A change in the composition of the mixtures toward one of the isomeric forms is evidently determined by a change in the nature of the radicals (increase in the induction effect) found at the γ-carbon atoms of the allylic halide system. Coupling products were also obtained in small amounts in the reactions of isomeric allylic halides with ethylmagnesium bromide and butylmagnesium bromide.

$$RO-CH_2-CH_2-\underset{\displaystyle CH=CH_2}{\underset{|}{CH}}-CH_2-CH=CH-CH_2-CH_2OR$$

In the present work we studied the reactions of organomagnesium compounds with the isomeric methoxychloroisohexenes, obtained by the addition of chloromethyl ether [6] to isoprene, and isoprene hydrochlorides. It could be postulated that an increase in the number of radicals on the γ-carbon atom in methoxychloroisohexenes when compared with methoxychloropentenes will lead to either the exclusive or predominant formation of products, corresponding in structure to the primary form of the allylic halide compound. Actually, when phenylmagnesium bromide was reacted with 1-methoxy-3-methyl-5-chloro-3-pentene we obtained only 1-methoxy-3-methyl-5-phenyl-3-pentene (I). The same product was also obtained in the similar reaction with 1-methoxy-3-methyl-3-chloro-4-pentene. In the last case the reaction proceeds with complete allylic rearrangement.

$$\left.\begin{array}{l} CH_3OCH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2Cl \\ CH_3OCH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CCl}}-CH=CH_2 \end{array}\right\} \xrightarrow{C_6H_5MgBr} CH_3OCH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-C_6H_5$$

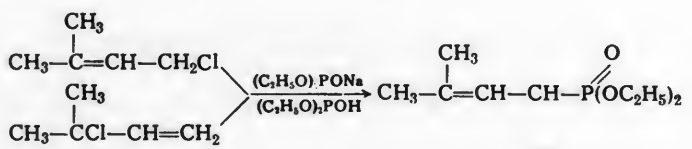
(I)

In the ozonolysis of (I) we identified phenylacetaldehyde as its dinitrophenylhydrazone. Similar results were also obtained in the reactions of 1-methoxy-3-methyl-5-chloro-3-pentene with ethylmagnesium bromide and butylmagnesium bromide; the products isolated were 1-methoxy-3-methyl-3-heptene and 1-methoxy-3-methyl-3-heptene and 1-methoxy-3-methyl-3-nonene, respectively. High-boiling products were not found. In the ozonolysis of the first we obtained butyraldehyde, identified as the dimedon derivative.

As the result of reacting 2-methyl-4-chloro-2-butene and 2-methyl-2-chloro-3-butene with phenylmagnesium bromide, we obtained the same product, namely, 2-methyl-4-phenyl-2-butene. The reaction of 2-methyl-4-chloro-2-butene with ethylmagnesium bromide gave only 2-methyl-2-hexene. Low-boiling fractions were obtained in a number of reactions, but we were unable to isolate any products with a definite boiling point from them.

As a result, it can be concluded that under the usual conditions of the Grignard synthesis the primary allylic halide isomers with two substituents on the γ-carbon atom react normally with organomagnesium compounds without any rearrangements, while tertiary allylic halides react with complete allylic rearrangement. Taking the results of previous investigations into consideration, we came to the conclusion that the reactions studied by us can be regarded as also proceeding by an ionic mechanism. A paper by R. Ya. Levina and co-workers [7] appeared while we were making the present study, in which the reactions of organomagnesium compounds with mixtures of isomeric isoprene hydrobromides were described. When reactions were run under usual conditions, they obtained products that corresponded to the primary bromide in structure, and in a number of cases they obtained both isomers of the hydrocarbon when the reaction was run at low temperature (−70°). It is quite probable that at low temperatures the reactions of allylic halide isomers with organomagnesium compounds also proceed more or less by a bimolecular mechanism.

In conclusion we studied the reactions of isomeric isoprene hydrohalides and 1-methoxy-3-methyl-5-chloro-3-pentene with sodium diethyl phosphite. Earlier we had shown that primary allylic halide isomers with one substituent on the γ-carbon atom react normally with sodium diethyl phosphite, while secondary allylic halide isomers react with complete allylic rearrangement. In the absence of free diethylphosphorous acid in the reaction mixture, and use of small amount of solvent in the reaction, a molecule of the diethylphosphorous acid adds to the unsaturated phosphinic ester with the formation of the diphosphonic derivative [8]. When the reactions of sodium diethyl phosphite with the isomeric hydrochlorides of isoprene were run in the presence of excess diethylphosphorous acid the same product was obtained in both cases, namely 2-methyl-4-diethylphosphono-2-butene (II). The reaction proceeds normally with the primary hydrochloride, while with the tertiary compound it proceeds with complete allylic rearrangement.



(II)

When the reaction of sodium diethyl phosphite with the tertiary hydrochloride of isoprene was run in the absence of free diethylphosphorous acid, we again obtained only (II) in the reaction mixture. Evidently the presence of two methyl groups on the γ-carbon atom of an allylic halide system not only secures a substantial shift of the electrons toward the α-carbon atom, but it also creates definite steric hindrance for the addition of the diethylphosphorous acid to the double bond of the unsaturated phosphinic ester. Similar steric hindrance was indicated by us also in the addition of dialkylphosphorous acids to unsaturated ketones and esters of unsaturated carboxylic acids, having two substituents on the γ-carbon atom [9].

EXPERIMENTAL

The isomeric methoxychloroisohexenes were prepared by the addition of chloromethyl ether to isoprene [6], while the hydrochlorides of isoprene were obtained by the addition of hydrogen chloride to isoprene.

Reaction of Phenylmagnesium Bromide with 1-Methoxy-3-methyl-5-chloro-3-pentene. To the Grignard reagent from 7.8 g of magnesium was added 40 g of 1-methoxy-3-methyl-5-chloro-3-pentene and the reaction

mixture was heated on the water bath for 4 hours. After treatment with water and dilute hydrochloric acid the ether layer was dried over calcium chloride, the ether was distilled off, and the residue was vacuum-distilled through a Widmer column. As the result of several distillations, we obtained 18 g of 1-methoxy-3-methyl-5-phenyl-3-pentene.

B. p. 121-122° for 8 mm, n_D^{20} 1.5100; d_4^{20} 0.9420, MR_D 60.33; calc. 59.80.

Found %: C 81.80; H 9.74. $C_{13}H_{18}O$. Calculated %: C 82.10; H 9.47. Unsaturation according to McIlhiney, 84%.

During distillation we also obtained a low-boiling fraction, which consisted of the starting chloride, and a number of fractions with wide boiling range.

Ozonolysis of 1-Methoxy-3-methyl-5-phenyl-3-pentene. Ozonized oxygen was passed for 24 hours through a solution of 5 g of 1-methoxy-3-methyl-5-phenyl-3-pentene in 40 ml of carbon tetrachloride with cooling in a cooling mixture. The carbon tetrachloride was removed in vacuo, and the ozonide was decomposed by heating with water. Phenylacetaldehyde was shown to be present, identified as the 2-4-dinitrophenylhydrazone, m. p. 110° (from alcohol). Literature [10]: m. p. 110°.

Reaction of Phenylmagnesium Bromide With 1-Methoxy-3-methyl-3-chloro-4-pentene. To the Grignard reagent, prepared from 1.5 g of magnesium, 7.3 g of bromobenzene and 25 ml of ether, was added 8 g of 1-methoxy-3-methyl-3-chloro-4-pentene. The reaction mixture was heated for 3 hours and then treated as described in the preceding experiment. We obtained 1.5 g of fractions, boiling in the range 40-122° at 10 mm, and 3 g of 1-methoxy-3-methyl-5-phenyl-3-pentene; b. p. 122-124° at 10 mm, n_D^{20} 1.5120, d_4^{20} 0.9451.

Reaction of Ethylmagnesium Bromide With 1-Methoxy-3-methyl-5-chloro-3-pentene. An ether solution of ethylmagnesium bromide was prepared from 5.1 g of magnesium and 23.8 g of ethyl bromide. Addition of 27 g of the chloride the mixture was heated on the water bath for 8 hours. Distillation gave 4 g of a fraction with b. p. 80-161° (n_D^{20} 1.4220) and 18 g of 1-methoxy-3-methyl-3-heptene.

B. p. 162-163° at 760 mm, n_D^{20} 1.4300, d_4^{20} 0.8151, MR_D 45.00; calc. 44.93.

Found %: C 75.64; H 12.41. $C_9H_{18}O$. Calculated %: C 76.05; H 12.67. Unsaturation according to McIlhiney, 91.7%.

Ozonolysis of 1-Methoxy-3-methyl-3-heptene. For ozonolysis we took 5 g of the hydrocarbon in 40 ml of dry carbon tetrachloride with cooling in a cooling mixture. After decomposition of the ozonide the butyraldehyde in the distillate was identified as its condensation product with dimedon, m. p. 136°.

Reaction of Butylmagnesium Bromide With 1-Methoxy-3-methyl-5-chloro-3-pentene. To an ether solution of butylmagnesium bromide, prepared from 6.8 g of magnesium and 32 g of butyl bromide, was added 34 g of the chloride. Distillation gave a fraction with b. p. 70-86° at 11 mm, consisting mainly of unchanged chloride, and 7 g of 1-methoxy-3-methyl-3-nonene.

B. p. 86-87° at 11 mm, n_D^{20} 1.4390, d_4^{20} 0.8233, MR_D 54.28; calc. 54.17.

Found %: C 77.31; H 12.98. $C_{11}H_{22}O$. Calculated %: C 77.64; H 12.94. Unsaturation according to McIlhiney 94.3%.

Ozonolysis of 1-methoxy-3-methyl-3-nonene yielded caproaldehyde, identified as its condensation product with dimedon, m. p. 104-106°.

Reaction of Phenylmagnesium Bromide With Isomeric Chloroisopentenes. Reaction with 1-Chloro-3-methyl-2-butene. An ether solution of phenylmagnesium bromide (5.4 g magnesium, 25.8 g bromobenzene) was treated with 28 g of the chloride. We obtained 17 g of 1-phenyl-3-methyl-2-butene.

B. p. 79-80° at 8 mm, n_D^{20} 1.5110, d_4^{20} 0.8971, MR_D 48.77; calc. 48.93. Literature data: b. p. 92° at 15 mm, $n_D^{18.3}$ 1.5125.

Reaction With 3-Methyl-3-chloro-1-butene. An ether solution of phenylmagnesium bromide (3.5 g magnesium, 16.3 g bromobenzene) was treated with 17.7 g of the chloride. Heating was continued for 3 hours. We obtained 1.5 g of a fraction with b. p. 25-75° at 8 mm and 7 g of 1-phenyl-3-methyl-2-butene with b. p. 78.5-79° at 8 mm, n_D^{20} 1.5118; d_4^{20} 0.8954.

Reaction of Ethylmagnesium Bromide With 1-Chloro-3-methyl-2-butene. An ether solution of ethylmagnesium bromide (3.7 g magnesium, 17.7 g ethyl bromide, 40 ml ether) was treated with 19 g of 1-chloro-3-methyl-2-butene. After several fractional distillations we obtained 7 g of 2-methyl-2-hexene.

B. p. 92-93 at 750 mm, n_D^{20} 1.4120. Unsaturation, according to McIlhiney, 97.7%.
Literature data [7]: b. p. 94-94.5° (755 mm), n_D^{20} 1.4127.

Reaction of Sodium Diethyl Phosphite With 1-Chloro-3-methyl-2-butene. An ether solution of sodium diethyl phosphite was prepared from 5.1 g of sodium, 31 g of diethylphosphorous acid and 230 ml of anhydrous ether. Then 30 g of 1-chloro-3-methyl-2-butene was added gradually, and the reaction mixture was heated for 3 hours on the water bath. The precipitate of sodium chloride was filtered, the ether distilled off, and the residue vacuum-distilled. We obtained 29 g of 1-diethylphosphone-3-methyl-2-butene.

B. p. 117-118° at 13 mm, n_D^{20} 1.4450, d_4^{20} 1.0080, MR_D 54.38. calc. 54.16.
Found %: P 15.27. $C_9H_{19}O_3P$. Calculated %: P 15.04. Unsaturation according to McIlhiney, 100%.

The ozonolysis of 1-diethylphosphono-3-methyl-2-butene yielded acetone, identified as the 2,4-dinitrophenylhydrazone, m. p. 124-125°.

Reaction of Sodium Diethyl Phosphite With 3-Chloro-3-methyl-1-butene. Expt. 1. An ether solution of sodium diethyl phosphite, prepared from 2.4 g of sodium, 28 g of diethylphosphorous acid and 100 ml of ether, was treated with 14 g of 3-chloro-3-methyl-1-butene. The reaction mixture was heated for 3 hours on the water bath; the separation of sodium chloride proceeded very slowly. Fractional distillation gave about 7 g of unchanged chloride, 7.4 g of diethylphosphorous acid and 5.8 g of 1-diethylphosphono-3-methyl-2-butene.
B. p. 111-112° at 8 mm, n_D^{20} 1.4430, d_4^{20} 1.009.

Expt. 2. A benzene solution of sodium diethyl phosphite (3.2 g sodium, 20 g diethylphosphorous acid and 32 ml benzene) was treated with 16 g of 3-chloro-3-methyl-1-butene. The same as in the preceding experiment, we isolated unchanged chloride, a low-boiling fraction, and 1-diethylphosphono-3-methyl-2-butene (5 g). High-boiling products were not found.

Reaction of Sodium Diethyl Phosphite With 1-Methoxy-3-methyl-5-chloro-3-pentene. An ether solution of sodium diethyl phosphite (4.4 g sodium, 27 g diethylphosphorous acid, 200 ml ether) was treated with 25.6 g of the chloride. The reaction mixture was heated on the water bath for 3 hours. We obtained 4 g of a fraction with b. p. 40-140° at 8 mm and 8 g of 1-methoxy-3-methyl-5-diethyl-phosphono-3-pentene.

B. p. 140-142° at 8 mm, n_D^{20} 1.4530, d_4^{20} 1.031, MR_D 65.58; calc. 65.04.
Found %: P 12.45. $C_{11}H_{23}O_4P$. Calculated %: P 12.40. Unsaturation 83.3%.

SUMMARY

1. It was shown that the primary allylic halides 1-methoxy-3-methyl-5-chloro-3-pentene and 1-chloro-3-methyl-2-butene react normally with ethyl-, butyl- and phenylmagnesium bromides under the usual conditions of Grignard syntheses, without allylic rearrangement, while the tertiary halides 1-methoxy-3-methyl-3-chloro-4-pentene and 2-methyl-2-chloro-3-butene react with complete allylic rearrangement.

2. The reactions of sodium diethyl phosphite with the isomeric hydrochlorides of isoprene and 1-methoxy-3-methyl-5-chloro-3-pentene were studied. The reactions with the primary allylic halide isomers proceed without rearrangement with the formation of esters of phosphinic acids, corresponding in structure to the starting chlorides, while with the tertiary allylic halides the reactions proceed with complete allylic rearrangement.

LITERATURE CITED

[1] A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1948, 24.

[2] C. Prevost, Comptes rend. 187, 946 (1928).

[3] C. Prevost, J. Daujat, Bull. Soc. Chim. 47, 588 (1930).

[4] A. Henne, H. Turk. J. Am. Chem. Soc. 63, 3474 (1941).

[5] A. N. Pudovik and G. M. Vinokurova, J. Gen. Chem. 19, 1882 (1949).*

[6] A. N. Pudovik and N. Altunina, J. Gen. Chem. 26, 1635 (1956).*

[7] R. Ya. Levina, V. R. Skvarchenko and T. M. Ushakova, J. Gen. Chem. 26, 398 (1956).*

[8] A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1949, 522; A. N. Pudovik and M. M. Frolova, J. Gen. Chem. 22, 2052 (1952).

[9] A. N. Pudovik, Prog. Chem. 23, 547 (1954).

[10] Brady, J. Chem. Soc. 1931, 756.

Received October 1, 1956

Kazan State University

*Original Russian pagination. See C. B. Translation.

DEALKYLATION OF ISOMERIC TRIBUTENYL PHOSPHITES WITH HYDROGEN CHLORIDE

A. N. Pudovik

Earlier we had described [1] the reaction of phosphorus trichloride with the isomeric butenols and ethoxypentenols. We postulated that complete esters of phosphorous acid are formed as intermediate products in these reactions, which then suffer dealkylation by the hydrogen chloride.

V. S. Abramov and G. A. Karp [2] made some critical remarks in connection with this work which, in our opinion, are completely unjustified. It is well known that the reaction of alcohols with phosphorus trichloride in the presence of bases, tying up the hydrogen chloride liberated during reaction, leads to the formation of complete esters of phosphorous acid, and in the absence of bases – to the formation of dialkylphosphorous acids. We see no postulation in this fact, utilized by us. During the last 50 years all of the chemists, working in the field of organophosphorus compounds, in their investigations with aliphatic phosphites have utilized the A. E. Arbuzov rearrangement scheme [3] with success, and in not a single case did doubts arise as to the validity of such utilization, even though the addition products of alkyl halides and hydrogen halides to aliphatic phosphites have not been isolated up to now. The remarks made by Abramov and Karp relative to allylic rearrangements are due to some misunderstanding. If the reaction of hydrogen chloride with primary and secondary butenols or with ethoxypentenols leads to the formation of mixtures of chlorides that are close in composition, then it is quite obvious that these reactions proceed with allylic rearrangement [4]. Allylic rearrangements cannot take place in the reactions of phosphorus trichloride with allylic alcohols, since only the oxygen-hydrogen bonds are involved in these reactions, and not the oxygen-carbon bonds of unsaturated alcohols. It is known that the esterification of unsaturated alcohols, in which the oxygen-hydrogen bond of the hydroxyl group of the alcohol participates, proceeds without allylic rearrangement [5].

To obtain greater conviction for our conclusions [1] and to further expand the study, we synthesized the complete esters of phosphorus acid having unsaturated radicals and studied their dealkylation with hydrogen chloride. Parallel with this, under the same conditions, we reacted phosphorus trichloride with butenyl, allyl and butyl alcohols.

When phosphorus trichloride was reacted with n-butyl alcohol and hydrogen chloride with tributyl phosphite, we obtained a good yield of n-dibutylphosphorous acid in both cases. When phosphorus trichloride was reacted with allyl alcohol, a 42% yield of diallylphosphorous acid was obtained [6]. In the experiment with triallyl phosphite about 1.3 allyl groups suffered dealkylation. Here the yield of diallylphosphorous acid was 45%.

In similar experiments between phosphorus trichloride, crotyl alcohol and methylvinylcarbinol we obtained mixtures of the isomeric chlorides and phosphorous acid in amounts close to the theoretical when calculated on the complete dealkylation of the intermediately formed complete and acid esters of phosphorous acid. With crotyl alcohol the mixture of chlorides by precise analysis consisted of 85% 1-chloro-2-butene and 15% 2-chloro-3-butene, while in the case of methylvinylcarbinol the mixture analyzed 56% 1-chloro-2-butene and 44% 2-chloro-3-butene. The calculations were based on the refractive indices of the mixtures and in some cases on the distillation data.

The reaction of tricrotyl phosphite with hydrogen chloride gave a mixture of chlorobutenes, consisting of 86% 1-chloro-2-butene and 14% 2-chloro-3-butene. The yield of phosphorous acid was 95.2%. In similar experiments, run with tri(α-methylallyl) phosphite, the yield of mixed butenyl chlorides was about 83% (when calculated

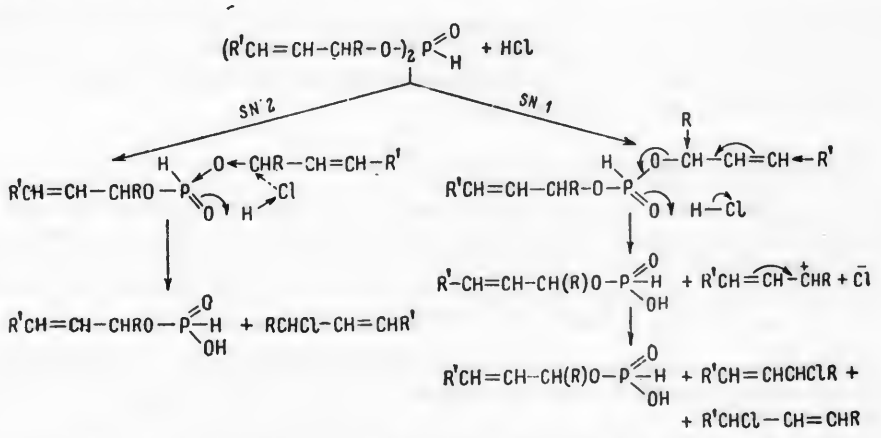
on the basis of complete dealkylation of the phosphite). Based on the data of a number of experiments, the mixture of chlorides consisted of 50-53% 1-chloro-2-butene and 47-50% 2-chloro-3-butene. The yield of phosphorous acid was 89.3%. The dealkylation of the phosphites with hydrogen chloride was studied in ether solution. The concentration of the phosphite was 0.1 N, and that of the hydrogen chloride was 0.5 N. The reactions were run at room temperature [7].

After three days the number of ester groups removed by dealkylation were: for tributyl phosphite 0.96, triallyl phosphite 1.7, tricrotyl phosphite 2.3, and tri(α-methylallyl) phosphite 2.2.

From the presented data in can be seen that the neutral and acid esters of phosphorous acid differ greatly in their tendency to dealkylate, which tendency is a direct function of the nature of the ester radicals. Also very important is the fact that the mixtures of isomeric chlorobutenes, formed in the dealkylation of tricrotyl phosphite and tri(α-methylallyl) phosphite, are very close in composition to the mixtures obtained in the reactions of phosphorus trichloride with crotyl alcohol and methylvinylcarbinol.

The obtained results serve to support our conclusion [1] that the reactions between phosphorus trichloride and butenyl alcohols proceed through the intermediate formation of phosphorous esters. A difference in the composition of the butenyl chlorides formed in the dealkylation of isomeric tributenyl phosphites was explained by us as being due to the fact that these reactions proceed by a mixed ionic-molecular mechanism in all of the phases of dealkylation. In the first phase, according to present concepts, the hydrogen chloride adds to the phosphite through its unshared electron pair, and then the addition product decomposes with the liberation of a mixture of butenyl chlorides and dibutenylphosphorous acid [3]. Data on the mechanism of the dealkylation of partial esters of phosphorous acid are completely lacking in the literature. We believe that this process is linked either with a preliminary tautomeric transformation of the forms containing pentavalent phosphorus into forms containing trivalent phosphorus, which then suffer dealkylation by the earlier presented schemes [1], or with a direct reaction of the hydrogen chloride on the dibutenylphosphorous acids containing pentavalent phosphorus. That the dialkylphosphorous acids are capable of tautomerization is indicated by their infrared [8] and Raman [9] spectra, the formation of complex compounds with potassium chloroplatinate [10] and the addition of sulfur to them at elevated temperatures (100-105°) in dioxane medium [11]. However, the dialkylphosphorous acids apparently contain a very small amount of the forms with trivalent phosphorus under ordinary conditions.

It is also necessary to keep in mind that dialkylphosphorous acids, containing primary and secondary radicals, are dealkylated only with great difficulty by hydrogen chloride at the reaction temperature (−10 to −15°). For this reason it is very probable that the ease and rapidity with which the dicrotylphosphorous and diisobutenylphosphorous acids are dealkylated under the indicated conditions is associated with the direct action of hydrogen chloride on the forms with pentavalent phosphorus.



Tricrotyl phosphite, R = H and R' = CH_3; triisobutenyl phosphite, R = CH_3 and R' = H.

The ratio of the reaction rates, proceeding by the SN 1 and SN 2 mechanisms, is determined by the structure of the unsaturated radicals found in the phosphite. Further dealkylation of acid esters, by a similar scheme, leads

to the formation of phosphorous acid. According to this mechanism the tendency of partial esters of phosphorous acid to dealkylate should be found directly related to the effectiveness of electron shift in the ester radicals; an enhanced shift will facilitate the formation of a bond between the oxygen of the phosphinic group and the hydrogen chloride, and consequently will facilitate dealkylation. This viewpoint permits explaining the greater tendency shown by dibutenylphosphorous acids to dealkylate when compared with diallylphosphorous acid, and that of the latter when compared with dialkylphosphorous acids. In connection with this it is interesting to mention that the reaction between phosphorus trichloride and tert-butyl alcohol proceeds similar to the butenyl alcohols and leads to the formation of phosphorous acid and tert-butyl chloride [7]. In the last case it is also possible to assume that the dealkylation of the acid ester formed during reaction is facilitated by the large induction effect of the three methyl groups in the ester radicals.

EXPERIMENTAL

Synthesis of Tricrotyl Phosphite. To 64.8 g of freshly distilled crotyl alcohol, 109 g of dimethylaniline and 250 ml of absolute ether, with cooling and stirring, was gradually added 41.3 g of phosphorus trichloride. The reaction mixture was stirred for 1 hour, and the precipitate of dimethylaniline hydrochloride was filtered and washed several times with absolute ether. Two fractional distillations of the filtrate gave 45.5 g of tricrotyl phosphite.

B. p. 98-99° (1 mm), d_4^{20} 0.9757; n_D^{20} 1.4680, MR_D 69.55; calc. 69.29.
Found %: P 13.11. $C_{12}H_{21}O_3P$. Calculated %: P 12.70.

Reaction of Phosphorus Trichloride With Alcohols

Crotyl Alcohol. To 50 g of crotyl alcohol, cooled to −15°, was slowly added 37 g of phosphorus trichloride with stirring. The reaction mixture was then stirred for another 30 minutes, and the upper layer was decanted from the precipitate, washed with water, then with dilute soda solution, and finally dried over calcium chloride. The weight of crude chlorides was 59.5 g, and that of phosphorous acid was 19 g. Distillation through A Widmer column, followed by distillation of the residue from a small Arbuzov flask with column gave 55.6 g of a fraction.

B. p. 64-84°, n_D^{20} 1.4320.
1-Chloro-2-butene has b. p. 84° (760 mm), n_D^{20} 1.4350; 2-chloro-3-butene has b. p. 64° (760 mm), n_D^{20} 1.4150.

Methylvinylcarbinol. When the experiment was run with 35.7 g of methylvinylcarbinol, we obtained a mixture of chlorides with n_D^{20} 1.4230. Distillation of the mixture gave 12.3 g of 2-chloro-3-butene and 18.6 g of 1-chloro-2-butene.

n-Butyl and Allyl Alcohols. The reactions were run by the procedure described in the preceding experiments. The experiment with n-butyl alcohol gave an 84% yield of dibutylphosphorous acid. When the reaction was run with allyl alcohol [6], the yield of diallylphosphorous acid was 42%. A large amount of residue remained in the flask, which on further heating exploded violently.

Reaction of Hydrogen Chloride With Phosphites

Tributyl Phosphite. A stream of dry hydrogen chloride was passed with cooling (−10 to −15°) into a cylinder containing 30 g of tributyl phosphite. Here 12.8 g was absorbed. The reaction mixture was allowed to stand for 30 minutes and then it was vacuum-distilled. At 30-40° and a pressure of 230 mm we obtained 10.7 g of n-butyl chloride. The saponification of one butyl group should have liberated 11.1 g of n-butyl chloride. Distillation of the residue gave 18.9 g of n-dibutylphosphorous acid.

Triallyl Phosphite. A stream of dry hydrogen chloride was passed through 10 g of triallyl phosphite with cooling (cooling mixture). After 4.9 g had been absorbed the reaction mixture was allowed to stand in the cooling mixture for 30 minutes. There was no precipitate. Fractional distillation of the reaction mixture gave 4.5 g of allyl chloride and 3.6 g of diallylphosphorous acid with b. p. 97-98° (8 mm), n_D^{20} 1. 4430. A large amount of undistillable residue remained in the flask.

Tri(α-methylallyl) Phosphite. Dry hydrogen chloride was passed into 10 g of the phosphite with cooling until 4.2 g had been absorbed. After standing for 30 minutes the liquid was decanted from the phosphorous acid

formed in the reaction, washed with water, dried over calcium chloride and distilled. We obtained 6.4 g of mixed butenyl chlorides, boiling in the range 64-84°, n_D^{20} 1.4256. The phosphorous acid was pressed and dried in a vacuum-desiccator. We obtained 3 g of phosphorous acid as compared to theory of 3.36 g (on the basis of complete dealkylation of the phosphite).

In a similar experiment with larger amounts of phosphite we obtained mixtures of the chlorides with n_D^{20} 1.4254 and 1.4250.

Tricrotyl Phosphite. The experiment was run the same as the preceding. From 10 g of tricrotyl phosphite we obtained 6.5 g of mixed chlorobutenes with n_D^{20} 1.4322 (in another experiment n_D^{20} 1.4326) and 3.2 g of phosphorus acid.

Dealkylation of Phosphites With Hydrogen Chloride in Ether Solution. The experiments on the dealkylation of tributyl phosphite, triallyl phosphite, tri(α-methylallyl) phosphite and tricrotyl phosphite were run simultaneously. From 70 to 80 ml of ether was poured into graduated cylinders and then treated with dry hydrogen chloride. After 1.8-2 g of HCl had dissolved (the amount in the ether solution was determined by titration of an aliquot with NaOH solution), the phosphite was added in such amount that its concentration was 0.1 N, and ether was added to give an HCl concentration of 0.5 N. The mixtures were stirred and allowed to stand at room temperature (18-20°). At predetermined time intervals 5 ml samples were removed and introduced into small flasks containing water. $AgNO_3$ solution was added after shaking the flask, and the chloride was determined by Volhard titration.

SUMMARY

The dealkylation of tri-n-butyl phosphite, triallyl phosphite, tricrotyl phosphite and tri(α-methylallyl) phosphite with hydrogen chloride was studied without solvent and in ether solution. Parallel with this a study was made of the reactions between phosphorus trichloride and the alcohols: n-butyl, allyl, crotyl and methylvinylcarbinol. The results proved to be identical in all cases. Dibutylphosphorous acid was obtained in good yield in the dealkylation of tributyl phosphite and when n-butyl alcohol was reacted with phosphorus trichloride; diallylphosphorous acid was obtained but in moderate yield, in similar experiments with allyl alcohol and triallyl phosphite, while mixtures of isomeric chlorides and phosphorous acid, quite close in composition, were obtained in the experiments with the isomeric butenols and tributenyl phosphites.

2. Tributenyl phosphites are the intermediate products in the reactions of phosphorus trichloride with butenols. Their primary dealkylation proceeds by the Arbuzov rearrangement scheme; opinions were expressed on the possible mechanisms for the further dealkylation of acid esters of phosphorous acid under the influence of hydrogen chloride.

M. V. Ivanova participated in the experimental portion of this study.

LITERATURE CITED

[1] A. N. Pudovik, Proc. Acad. Sci. USSR 84, 519 (1952).

[2] V. S. Abramov and G. A. Karp, J. Gen. Chem. 24, 1823 (1954).*

[3] A. E. Arbuzov, "Structure of Phosphorous Acid and Its Derivatives," Dissertation, New Alexandria, 1905.**

[4] J. Meisenheimer and J. Link, Lieb. Ann. 479, 211 (1950).

[5] C. Prevost, and A. Kirrman, Bull. Soc. Chim. 49, 194 (1931); A. N. Pudovik and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 541.

[6] G. Kh. Kamai and E. I. Shugurova, J. Gen. Chem. 21, 658 (1951).*

[7] W. Gerrard and E. Whitbread, J. Chem. Soc. 1952, 914.

[8] H. Cook, J. Chem. Soc. 1949, 2921.

[9] A. E. Arbuzov, M. I. Batuev and V. S. Vinogradova, Proc. Acad. Sci. USSR 54, 603 (1946)

[10] A. A. Grinberg and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1944, 178; A. A. Grinberg, Proc. Acad. Sci. USSR 105, 1256 (1955).

[11] M. I. Kabachnik and E. I. Golubeva, Proc. Acad. Sci. USSR 105, 1258 (1955).

Received May 25, 1956

Kazan State University

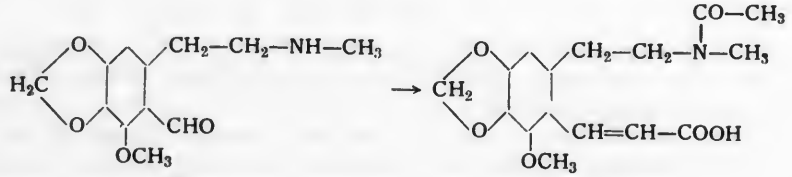
* Original Russian pagination. See C. B. Translation.
** In Russian.

PROBLEMS IN THE STRUCTURE OF COTARNINE DERIVATIVES

III. STRUCTURE OF "HYDROCOTARNINEACETIC ACID"

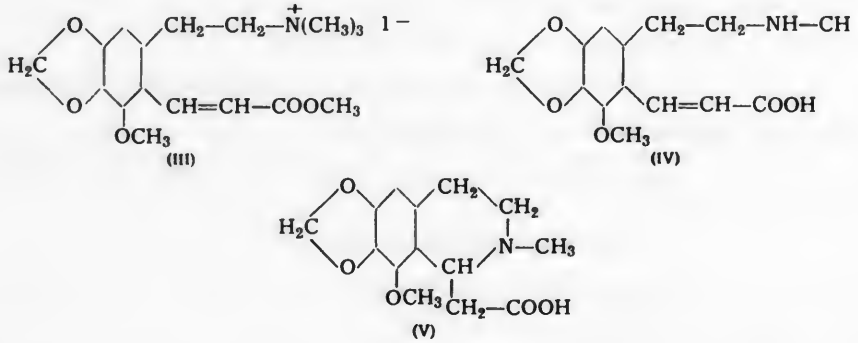
Denesh Beke, Kalman Kharshani and Iene Kereshi

Cotarnine reacts with acetic anhydride [1, 2] to form 6-methoxy-4,5-methylenedioxy -2-[β -(methylaceto-amino)ethyl]cinnamic acid, "acetylhydrocotarnineacetic acid" (II). This reaction is considered evidence of the aminoaldehyde structure (I) of cotarnine.



(I) (II)

By boiling "acetylhydrocotarnineacetic acid" with dilute hydrochloric acid it was possible to prepare in poor yield the hydrochloride of "hydrocotarnineacetic acid" [1], from which the silver salt was obtained by the use of silver oxide [3], and from the latter salt the free "hydrocotarnineacetic acid" was obtained by the action of hydrogen sulfide. By the reaction of the methyl ester of "hydrocotarnineacetic acid" with methyl iodide there was obtained [3] along with the hydroiodide of the ester the methiodide of the methyl ester of 6-methoxy-4,5-methylenedioxy-2-(β -dimethylaminoethyl)cinnamic acid (III). On this basis "hydrocotarnineacetic acid" is regarded in the literature as 6-methoxy-4,5-methylenedioxy-2-(β -methylaminoethyl)cinnamic acid (IV), thus ignoring the cyclic tautomeric form (V).

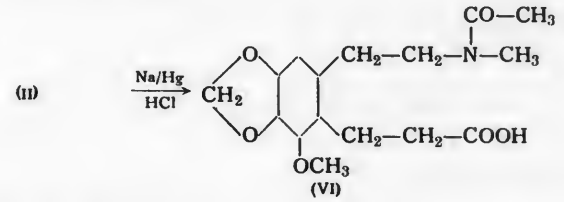


(III) (IV) (V)

As a result of our experiments it appears that "hydrocotarnineacetic acid" can be prepared from the acetyl derivative in very good yield and much more easily if the deacetylation is carried out with alkali of suitable

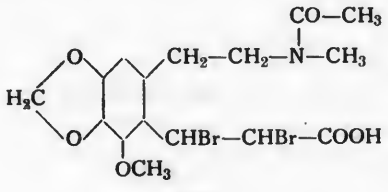
concentration instead of hydrochloric acid. V. A. Maslennikova and G. V. Lazuryevsky [4] have prepared this compound also directly from cotarnine by the use of Debner reagent, but they did not state either the experimental conditions or the yields. From our experiments it ensues that when cotarnine reacts with malonic acid in pyridine solution, it forms "hydrocotarnineacetic acid" in high yield.

To clarify its structure, we first tried to reduce "hydrocotarnineacetic acid;" but the reduction, which proceeds easily in the case of the acetylated acid [3], could not be brought about in this instance either by catalytic hydrogenation or by the use of 3% sodium amalgam.

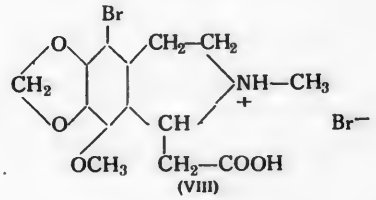


(VI)

In spite of the fact that the compound does not add hydrogen, it reacts readily with bromine; the bromine content of the product obtained (determined by fusion with potassium hydroxide or by the Carius method) corresponds to the addition of two atoms of bromine: one of the bromine atoms is in the ionic state and can be directly titrated with silver nitrate in aqueous solution. While the N-acetyl derivative with the open chain gives [3] the addition product (VII) with bromine, in the case of "hydrocotarnineacetic acid" substitution occurs, which also proceeds very easily in hydrocotarnine itself in position 5; the hydrogen bromide formed yields with the amino group of the compound the salt (VIII).



(VII)



(VIII)

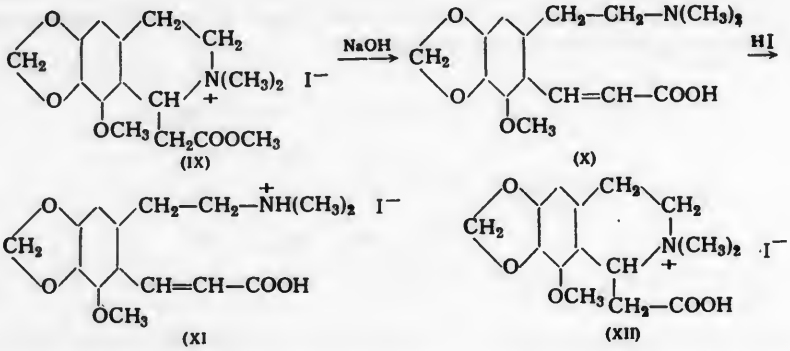
In order to identify the compound, we prepared from 5-bromocotarnine by the method of Debner "hydrocotarnineacetic acid" brominated in the 5 position, the hydrobromide of which appeared in all respects identical with the product obtained by the bromination of "hydrocotarnineacetic acid." The behavior of "hydrocotarnineacetic acid" in regard to hydrogenation and bromination can be explained only on the basis of the cyclic structure (V); the latter is substantiated also by spectroscopic examination in the ultraviolet. While the spectrum of the acetyl derivative shows an absorption maximum that is characteristic of styrene derivatives at 330 mμ, "hydrocotarnineacetic acid" and its hydrochloride show an absorption of a much lower order of magnitude, and in general no absorption maximum is observed for them at the wave length mentioned above (see figure).

Consequently, "hydrocotarnineacetic acid" is not 6-methoxy-4,5-methylenedioxy-2-(β-methylaminoethyl)cinnamic acid, but is 2-methyl-8-methoxy-6,7-methylenedioxy-1-carboxymethyl-1,2,3,4-tetrahydroisoquinoline, or more briefly 1-hydrocotarnylacetic acid.

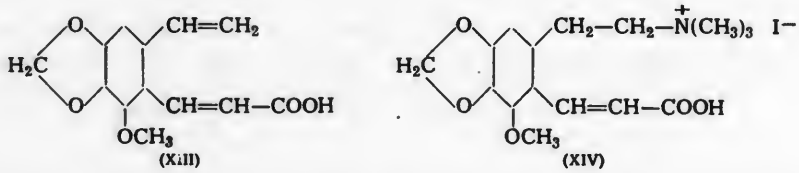
By heating the compound with acetic anhydride it was possible to obtain the N-acetyl derivative with the open chain. Consequently, the production of N-acyl derivatives with the open structure cannot serve as proof of the presence of a secondary amino group in cotarnine.

From the methyl ester of 1-hydrocotarnylacetic acid we prepared a methiodide with m. p. 119° described by Ahlers [3] by the action of methyl iodide. Closer study of this compound showed that its properties did not agree with the formula (III) adduced by Ahlers [3]; upon boiling with alkali, trimethylamine was not split out and the analytical data permitted the conclusion that the cyclic methiodide (IX) was formed as a result of the

addition of one molecule of methyl iodide. The cyclic structure of the compound was substantiated by us by an indirect method; the hydroiodide (XI) of the product (X), which was obtained from it by boiling with alkali was not identical with compound (XII), which was produced from 1-hydrocotarnylacetic acid by the addition of 1 mole of methyl iodide.



We also succeeded in obtaining the methiodide of the methyl ester of 6-methoxy-4,5-methylenedioxy-2-(β-dimethylaminoethyl)cinnamic acid with the open chain, which corresponds to the formula proposed by Ahlers, by the addition of 2 moles of methyl iodide both from the cyclic methiodide and from the methyl ester of 1-hydrocotarnylacetic acid by the action of excess methyl iodide and alkali. M. p. 199-200°; upon boiling with alkali the compound broke down into trimethylamine and an acid that did not contain nitrogen, which separated out when the alkaline solution was acidified. This acid did not give a depression in melting point with 2-vinyl-4,5-methylenedioxy-6-methoxycinnamic acid (XIII), which was described by V. M. Rodionov and M. G. Chentsova [5].



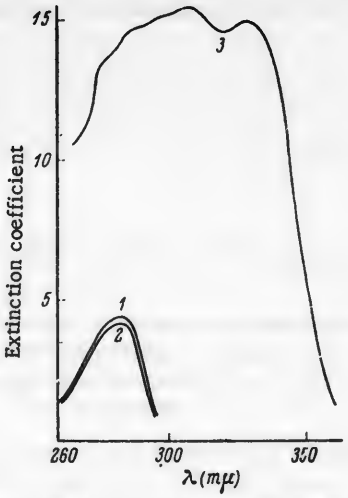
The structure of the methiodide (XII) which was produced by the addition of 1 mole of methyl iodide (from 1-hydrocotarnylacetic acid), and the methiodide with an open chain (XIV) which was produced by the action of an excess of methyl iodide in the presence of alkali, was proved by their behavior when they were boiled with alkali and by analytical data. Consequently, the cyclic methiodide was formed in the first stage of the reaction upon treatment with methyl iodide; the quaternary ammonium salt with the open chain was formed as a result of a secondary process of ring cleavage.

The preparation of 1-hydrocotarnylacetic acid by the method of Debner conforms well with the cyclic structure for cotarnine. But neither the formation of "acetylhydrocotarnineacetic acid" from cotarnine and acetic anhydride, nor the formation of the methiodide with an open chain from the methyl ester of 1-hydrocotarnylacetic acid and methyl iodide presumes the aminoaldehyde form of cotarnine, since acetic anhydride and methyl iodide in the presence of alkali can bring about ring cleavage.

EXPERIMENTAL

6-Methoxy-4,5-methylenedioxy-2-(β-methylaminoethyl)cinnamic acid, 1-hydrocotarnylacetic acid, "hydrocotarnineacetic acid" (V)

a) 3.21 g of "acetylhydrocotarnineacetic acid" was refluxed with 25 ml of 10% sodium hydroxide for 1.5 hours. There precipitated from the raspberry-colored solution upon cooling the sodium salt of 1-hydrocotarnylacetic acid as white crystals with a silky luster, shaped like small needles. After standing for 1 hour in the cooling



Ultraviolet spectra of hydrocotarnineacetic acid and its derivatives.
1) Hydrocotarnineacetic acid hydrochloride; 2) hydrocotarnineacetic acid; 3) N-acetyl-hydrocotarnineacetic acid.

mixture (ice + sodium chloride) the crystals were washed with a small amount of alcohol. Yield 2.66 g (88.5%). After recrystallization from methyl alcohol, m. p. 224° (decomp.)

b) 23.73 g of cotarnine was heated with 20.80 g of malonic acid and 90 ml of pyridine for 1 hour at 105-110° in a round-bottomed flask with a reflux condenser; evolution of carbon dioxide began quickly and ended in 40-50 minutes. Only then the temperature of the oil bath was raised above the boiling point of pyridine and the reaction mixture was boiled for 1 hour, after which the pyridine was distilled off in vacuo. The red-brown residue dissolved upon heating in 200 ml of 15% sodium hydroxide solution; the sodium salt crystallized out upon cooling. After washing with a small amount of alcohol, the yield was 26.18 g (87%). After addition of the calculated amount of 10% hydrochloric acid to a solution of the sodium salt in twice the amount of hot water, the free 1-hydrocotarnylacetic acid separated out. It was crystallized from water as small white or colorless rhombic crystals, m. p. 116°. The crystals contained 2 moles of water of crystallization; the anhydrous 1-hydrocotarnylacetic acid melted at 203-204° (decomp.)

Found %: C 53.42; H 6.53; H_2O 1.16. $C_{14}H_{17}O_5N \cdot 2H_2O$. Calculated %: C 53.33; H 6.72; H_2O 1.15.

Reduction of 1-hydrocotarnylacetic acid. 13.5 g of sodium 1-hydrocotarnylacetate was dissolved in 135 ml of water and 296 g of 3% sodium amalgam (4.3-fold excess) was added with vigorous stirring over a period of 1 hour; at the same time 25 ml of concentrated hydrochloric acid was added to decrease the alkalinity of the mixture. After 2 hours' stirring the weakly alkaline solution was decanted from the mercury and after filtration it was acidified with hydrochloric acid (pH 3). The white, cottony crystals that precipitated were separated out and dried. Yield 12 g; after repeated recrystallization from water, m. p. 205-206° (decomp.) From the analytical data, the melting point of a mixed sample and the results of investigation of the product obtained after the addition of an equivalent amount of alkali, it was possible to establish that the hydrochloride of 1-hydrocotarnylacetic acid, which crystallized with 1 mole of water, was reversibly obtained.

Found %: C 50.44; H 6.06; N 4.33; Cl 10.42; H_2O 5.56. $C_{14}H_{17}O_5N \cdot HCl \cdot H_2O$. Calculated %: C 50.38; H 6.04; N 4.20; Cl 10.62; H_2O 5.39.

Attempts were made to catalytically hydrogenate both 1-hydrocotarnylacetic acid itself and its sodium salt and methyl ester. Addition of hydrogen was not observed either in ethyl acetate solutions, in methanol, in glacial acetic acid, in water solution in the presence of palladium on carbon, or in the presence of Raney nickel or platinum sponge (at STP).

Hydrobromide of 5-bromo-1-hydrocotarnylacetic acid (VIII). a) 3.16 g of 1-hydrocotarnylacetic acid (m. p. 116°), containing 2 moles of water of crystallization, was dissolved at 50° in 20 ml of glacial acetic acid; after the solution was cooled, a solution of 1.85 g of bromine in 2 ml of glacial acetic acid was added to it drop by drop; the bromine was decolorized immediately. After the reaction mixture was evaporated in vacuo, a yellowish white, lustrous crystalline powder separated, which was titrated with 2 × 10 ml of alcohol cooled with ice, and isolated. Yield 4 g (91%), m. p. 210-211° (decomp.); after recrystallization from aqueous alcohol, m. p. 220-222°.

Found %: Br 36.62 (Carius), 36.73 fusion with potassium hydroxide; HBr 18.42. $C_{14}H_{16}O_4NBr \cdot HBr$. Calculated %: Br 36.40; HBr 18.20.

b) A mixture of 3.17 g of 5-bromocotarnine, 2 g of malonic acid and 9 ml of pyridine was heated for 1 hour at 100-105°, then for 1 hour more at 120-125°; during this, copious evolution of carbon dioxide was

observed. The pyridine was removed under reduced pressure and the remaining reddish oil was dissolved by heating in 20 ml of 15% sodium hydroxide. Upon cooling 2.9 g (76.5%) of the crystalline sodium salt precipitated.

2.8 g of the sodium salt was dissolved by heating in 6 ml of water and to the still hot solution there was added a mixture of 0.6 ml of concentrated hydrochloric acid and 2 ml of water. Upon cooling, 2.1 g of 5-bromo-1-hydrocotarnylacetic acid precipitated, which melted at 200-201° (decomp.) after recrystallization from warm water and gave no depression with the acid obtained from the hydrobromide described in "a."

Found %: Br 22.13. $C_{14}H_{16}O_5NBr$. Calculated %: Br 22.31.

By conversion of the compound obtained to the hydrobromide, a material was produced that was identical with the hydrobromide described above in "a."

Methyl ester of 1-hydrocotarnylacetic acid. 1.58 g of 1-hydrocotarnylacetic acid containing water of crystallization was boiled for 2 hours on a water bath with 10 ml of anhydrous methanol containing hydrochloric acid. The filtered solution was evaporated to 6 ml and the hydrochloride of the methyl ester that crystallized out was separated. Yield 1.34 g (90%). After recrystallization from methanol, m. p. 220° (decomp.)

3.30 g of the hydrochloride was suspended in a separatory funnel with 10 ml of water and to it was added 4 ml of 10% sodium hydroxide solution. The clear oil that separated was extracted with ether, the ether solution was washed with water and dried with anhydrous sodium sulfate, then the ether was distilled off. Yield 2.15 g (73.5%); large, colorless crystals of laminar shape; after repeated recrystallization from methanol, m. p. 78-79° (m. p. according to [3] 63°).

Methiodide of methyl ester of 1-hydrocotarnylacetic acid (IX). 3.30 g of the methyl ester of the hydrochloride of 1-hydrocotarnylacetic acid was dissolved in 20 ml of water and the free ester was separated by the addition of 0.4 g of sodium hydroxide dissolved in 4 ml of water. 11.36 g of CH_3I was added to the reaction mass, after which it was refluxed for a half-hour. Even in the first minute fine, white needles began to precipitate. After the excess methyl iodide was distilled off, the remaining crystalline mass was cooled, separated and washed with water. Yield 3.65 g (80%). After recrystallization from water or alcohol, m. p. 119°; after removal of 1.5 moles of water of crystallization, m. p. 127-129°.

Found %: C 41.54; H 5.37; H_2O 0.61. $C_{16}H_{22}O_5NI \cdot 1.5\ H_2O$. Calculated %: C 41.57; H 5.45; H_2O 0.58.

Hydroiodide of 6-methoxy-4,5-methoxy-4,5-methylenedioxy-2-(β-dimethylaminoethyl)-cinnamic acid (XI). 0.90 g of the methiodide of the methyl ester of 1-hydrocotarnylacetic acid was heated with a mixture of 1 ml of water and 2 ml of 10% sodium hydroxide for 1.5 hours on a water bath; the transparent solution obtained was acidified after cooling with 5% hydriodic acid to pH 2. Upon cooling in a refrigerator 0.8 g (92%) of a crystalline product separated, which melted after recrystallization from methyl alcohol at 191-192° (decomp.)

Found %: C 43.05; H 4.66; I 30.32. $C_{15}H_{20}O_5NI$. Calculated %: C 42.77; H 4.79; I 30.17.

Methiodide of methyl ester of 6-methoxy-4,5-methylenedioxy-2- (β-dimethylaminoethyl)cinnamic acid (III). a) 3.30 g of the methyl ester of the hydrochloride of 1-hydrocotarnylacetic acid was refluxed with 10 ml of water, 5.68 g of methyl iodide and 0.88 g of NaOH dissolved in 4 ml of water for 1.5 hours. After cooling, the reaction mass was acidified with 10% hydrochloric acid (pH 3-4); an oily material separated that solidified very quickly in small granular crystals. After the material was separated and washed with a small amount of cold water, the yield was 3.06 g (68%). The product recrystallized from a mixture of acetate and methyl alcohol (2:1), melted at 199-200° (decomp.) Upon heating with sodium hydroxide a considerable evolution of trimethylamine was observed.

b) 0.30 g of the methiodide of the methyl ester of 1-hydrocotarnylacetic acid was heated with 1 ml of water. 1.14 g of methyl iodide, and 0.3 ml of 10% sodium hydroxide solution, after which the colorless solution was acidified with 10% hydrochloric acid (pH 3); a clear oil separated, which very quickly solidified upon cooling and rubbing. Yield 0.27 g (87%), melting point after recrystallization (see "a") 198-200° (decomp.)

Found %: C 45.45; H 5.32. $C_{17}H_{24}O_5NI$. Calculated %: C 45.44; H 5.38.

Methiodide of 1-hydrocotarnylacetic acid (XII). 1 g of 1-hydrocotarnylacetic acid containing water of crystallization was dissolved in 1.5 ml of water by heating; after the solution was cooled, 4.65 g of methyl iodide was added, after which the reaction mass was boiled for 2 hours. After the excess methyl iodide was distilled off, white crystals separated out from the yellowish solution in the refrigerator over a period of several days. After separation and washing with ethyl acetate, the yield was 0.62 g (40%). The melting point after recrystallization from a mixture of ethyl acetate and methanol (1 : 1) was 175-177° (decomp.) Upon heating with sodium hydroxide trimethylamine was not split out.

Found %: I 30.41. $C_{15}H_{20}O_5NI$. Calculated %: I 30.17.

Methiodide of 6-methoxy-4,5-methylenedioxy-2-(β-dimethylaminoethyl)-cinnamic acid (XIV). 1.58 g of 1-hydrocotarnylacetic acid containing water of crystallization was heated with a solution of 0.40 g of sodium hydroxide in 3 ml of water and with 4.56 g of methyl iodide on a water bath for 2 hours. After the excess methyl iodide was distilled off, the solution was acidified with 10% hydrochloric acid (pH 4) and the crystalline mass that was obtained upon cooling and rubbing the yellowish oil that separated was isolated and then washed with a small amount of water. Yield 1.90 g (87%). After recrystallization from 80% methanol, m. p. 235° (decomp.)

Found %: C 44.16; H 5.10. $C_{16}H_{22}O_5NI$. Calculated %: C 44.15; H 5.09.

Upon heating the compound with a sodium hydroxide solution, the odor of trimethylamine was detected; upon acidification of the alkaline solution a crystalline substance separated, which did not contain nitrogen, with m. p. 177-179°, which gave no lowering in melting point with 2-vinyl-4,5-methylenedioxy-6-methoxycinnamic acid (XIII) prepared according to the data of Rodionov and Chentsova [5].

We wish to thank G. Zemplen for his interest in our work, I. Batta for carrying out the analyses, and Yu. Varshani for plotting and deciphering the ultraviolet spectra.

SUMMARY

It has been shown that "hydrocotarnineacetic acid," which is referred to in the literature as 6-methoxy-4,5-methylenedioxy-2-(β-methylaminoethyl)cinnamic acid, does not contain a double bond; it is not reduced either by catalytic hydrogenation or by sodium amalgam; with bromine it does not yield an addition product but gives a substitution product; which facts can be explained only by a cyclic structure for the compound. The compound is 2-methyl-8-methoxy-6,7-methylenedioxy-1-carboxymethyl-1,2,3,4-tetrahydroisoquinoline, or, more briefly, 1-hydrocotarnylacetic acid.

By the action of acetic anhydride or of methyl iodide in the presence of sodium hydroxide, the nitrogen-containing ring of the compound is opened; consequently, the formation of "acetylhydrocotarnineacetic acid" from cotarnine and acetic anhydride as well as that of the methiodide of the methyl ester of 6-methoxy-4,5-methylenedioxy-2-(β-dimethylaminoethyl)cinnamic acid from the methyl ester of "hydrocotarnineacetic acid" by the action of the methyl iodide and sodium hydroxide is not explained on the basis of the aminoaldehyde form of cotarnine.

LITERATURE CITED

[1] W. Bowman, Ber. 20, 2431 (1887).

[2] C. Lieberman, F. Kropf, Ber. 37, 211 (1904).

[3] W. Ahlers, Ber. 38, 2873 (1905).

[4] V. A. Maslennikova and L. V. Lazuryevsky, Proc. Acad. Sci. USSR, 72, 305 (1950).

[5] V. M. Rodionov and M. G. Chentsova, J. Gen. Chem. 23, 1849 (1953).*

Received January 18, 1956

Budapest Polytechnic University

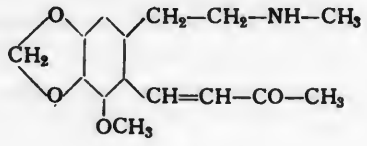
*Original Russian pagination. See C. B. Translation.

PROBLEMS IN THE STRUCTURE OF COTARNINE DERIVATIVES

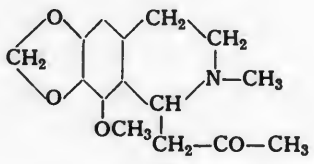
IV. STRUCTURE OF PRODUCTS OF THE CONDENSATION OF COTARNINE WITH ACETONE

Denesh Beke and Kalman Kharshani

The reaction of cotarnine with acetone was first studied by Lieberman and Kropf [1]. On reaction with acetone in the presence of a saturated solution of sodium carbonate, cotarnine forms a crystalline compound that melts at 83°, for which the authors mentioned above considered equally possible the cotarnylideneacetone structure with an open chain (I) and the cyclic 1-hydrocotarnylacetone structure (II).

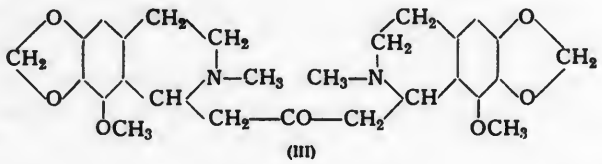


(I)



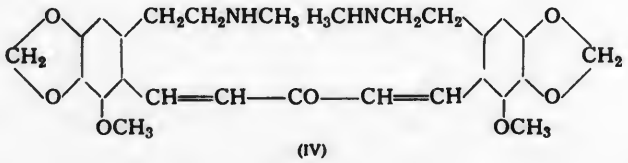
(II)

Dey and Kantam [2] carried out the reaction in alcohol solution and obtained in this manner a compound melting at 150-151°, to which they ascribed the structure 1,3-di-(1-hydrocotarnyl)acetone (III) on the basis of the analytical data and the chemical properties.



(III)

The substance obtained by Lieberman and Kropf, which melted at 83°, was taken by Dey and Kantam (on the basis of analytical data and the molecular weight, which were not determined in their work) to be dicotarnylideneacetone (IV), formed also by the reaction of 2 moles of cotarnine with 1 mole of acetone.



(IV)

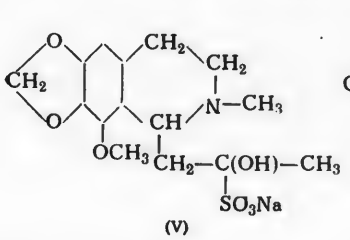
They based their opinion first of all on the fact that the compound which melted at 83° was converted after recrystallization from hot alcohol to a compound with m. p. 151°; they considered that this could serve as definite evidence of the ring-chain tautomerism of cotarnine and its derivatives, which also has been accepted in the later literature [3].

V. A. Maslennikova and G. V. Lazuryevsky [4] prepared compounds with m. p. 83° and 156° by the reaction of cotarnine with acetonedicarboxylic acid or acetoacetic acid, respectively; these synthesis definitely show that the first compound is the product of condensation of 2 moles of cotarnine with 1 mole of acetone, and the second is the product from 1 mole of cotarnine and 1 mole of acetone; but, apparently, their melting points were erroneously confused, as was shown after repetition of these experiments by us. Maslennikova and Lazuryevsky ascribed to both these compounds the open cotarnylidene form.

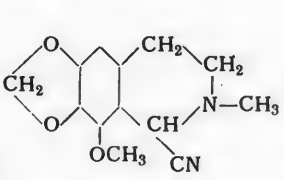
In order to finally clarify the structure of the products of the condensation of cotarnine with acetone, we prepared both compounds.

Determination of the molecular weight, carried out in benzene solution by the cryoscopic method, showed that the product with m. p. 83° is the compound formed by the reaction of 1 mole of cotarnine with 1 mole of acetone, and the substance melting at 151° according to the data given in [2], but at 156° according to the data in [4], (the melting point of which we were able to raise by repeated recrystallization to 162°) is the product of condensation of 2 moles of cotarnine with 1 mole of acetone. As additional evidence of this, we succeeded in converting the substance with m. p. 83° by reaction with cotarnine (in molar ratio in alcohol solution) into the compound with higher melting point and greater molecular weight (yield 73%). From the compound melting at 83° we obtained an addition product with sodium bisulfite (V), the sulfur content of which also indicated that we were dealing here with the product of condensation of 1 mole of cotarning with 1 mole of acetone. From the sodium bisulfite addition product it was possible to regenerate the starting ketone. The compound formed by the reaction of 2 moles of cotarnine with 1 mole of acetone did not give an addition product with sodium bisulfite, which is readily understood if we take into account the steric effect of the two substituents.

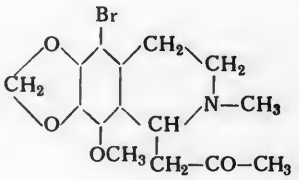
Consequently, the substance melting at 83° is converted to the substance with m. p. 151° not by isomerization, but by disproportionation; 1 mole of acetone is split off from 2 moles of the compound with m. p. 83°, with the formation of the compound of higher melting point. The correctness of this hypothesis also ensues from the fact that, according to our investigation, acetone is very easily split out from the compound upon heating with sodium bisulfite or by the action of hydroxylamine hydrochloride with the formation of sodium hydrocotarnine-1-sulfoxylate or cotarnine chloride, and also that the sodium bisulfite addition product (V) forms upon reaction with KCN 1-cyanohydrocotarnine (VI) instead of the cyanohydrin.



(V)

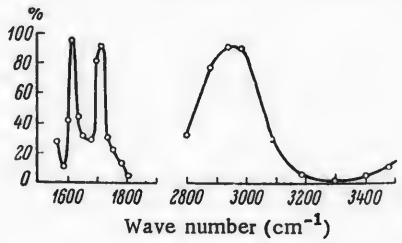


(VI)



(VII)

In order to clear up the question of whether the compounds have the cyclic structure or the open chain, we checked their behavior (as we also did that of 1-hydrocotarnylacetic acid [5]) in the process of catalytic hydrogenation and bromination. In the presence of animal charcoal on palladium neither of the compounds added hydrogen. Upon bromination of both compounds not addition but substitution in the 5 position occurred, which can be explained only by the cyclic structure for the compounds. For purposes of identification we prepared also 1-(5-bromohydrocotarnyl) acetone (VII) and its hydrobromide from 5-bromocotarnine and acetone; the two products, obtained by the two different methods, appeared to be identical according to a melting point test. Spectroscopic investigation in the infrared region, carried out in the Chemical Scientific-Research Institute of the Academy of Sciences of Czechoslovakia, also indicated the cyclic structure of the substance with m. p. 83°; the spectrum, determined in chloroform solution, had a maximum at the wave number* 1715, which is characteristic of the carbonyl

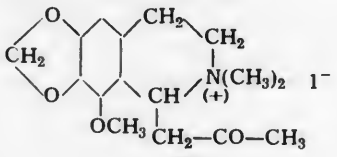


Infrared spectrum of 1-hydrocotarnylacetone (between wave numbers 1500-1900 and 2800-3500).

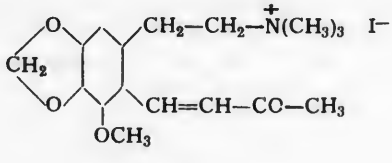
* Wave number is the number of waves per cm.

group and which excludes the presence of a double bond in a conjugated position to the carbonyl group that is characteristic of the open chain structure; also there was not seen the frequency characteristic of the NH group which appears in primary and secondary amines (within the limits of the wave numbers 3270-3460 or in the case of a hydrogen bond between 3050 and 3350).

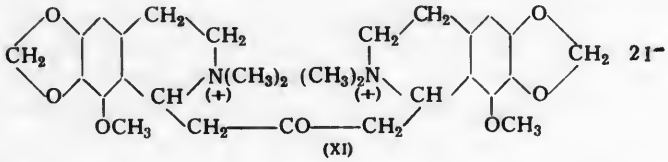
From the compounds melting at 83 and 162° it was possible to obtain the methiodides (IX-XII), both cyclic and open-chain. In the first stage of the reaction here also the cyclic methiodides were formed; but the quaternary ammonium salts with the open chain are formed as a result of a secondary process of ring cleavage just as in the case of 1-hydrocotarnylacetic acid.



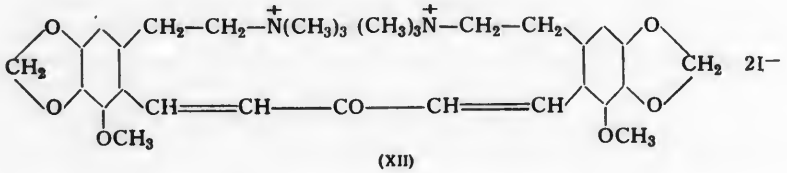
(IX)



(X)



(XI)



(XII)

On the basis of our previous investigations [5-7] and the results stated in the present communication, we have been able to establish that all of those cotarnine derivatives for which we might on principle propose a ring-chain tautomerism are actually cyclic compounds, and the open-chain derivatives (quaternary ammonium salts and N-acyl derivatives) as though obtained from the hypothetical aminoaldehyde form are produced as a result of opening of the ring in the cyclic compounds. All the reactions of cotarnine agree well with the cyclic structure.

Consequently, in the case of cotarnine it is not possible to maintain the generally accepted view [8] that the pseudo-basic 2-carbinols are members of such ring-chain prototropic systems in which the aminoaldehyde is a second tautomer.

EXPERIMENTAL

1-Hydrocotarnylacetone (II). 20 g of cotarnine was shaken for 1 hour with 60 ml of acetone and 1 ml of saturated sodium carbonate solution; then the mixture was allowed to stand at room temperature for 30-36 hours, after which a clear solution was obtained. On the following day 40 ml of acetone was distilled off from the reaction mixture and the residue was diluted with 100 ml of water. 1-Hydrocotarnylacetone separated as a thick oil which solidified upon rubbing in the course of several days. By recrystallization from light benzene (b. p. 40-100°) 19.8 g (85%) was obtained of a compound with m. p. 83°.

Found %: C 65.37; H 6.78; N 5.00. M 284(in benzene). $C_{15}H_{19}O_4N$. Calculated %: C 65.11; H 6.91; N 5.05. M 277.31.

Reaction of 1-hydrocotarnylacetone with sodium bisulfite. 1.39 g of finely pulverized 1-hydrocotarnylacetone was added to a solution of 4 g of $NaHSO_3$ in 10 ml of water; upon shaking, a clear solution was obtained at

at first, from which there separated in a short time a large amount of a white, crystalline precipitate. After 5 hours standing in a refrigerator, filtration with suction and washing with ice water, 1.85 g (97%) of compound (V) was obtained, which melted after recrystallization from alcohol at 120-122° (decomp.)

Found %: N 4.10; S 8.17. $C_{15}H_{20}O_7NSNa$. Calculated %: N 3.67; S 8.41.

It was possible to regenerate 1-hydrocotarnylacetone from the compound in good yield by treatment with dilute alkali.

1.90 g of the sodium bisulfite addition product of 1-hydrocotarnylacetone was suspended in 10 ml of water and mixed with a solution of 0.5 g of KCN in 5 ml of water. A greasy precipitate formed, which solidified upon rubbing. After standing for 2-3 hours and filtration, 1.27 g of crude product was obtained that melted agter recrystallization from alcohol at 89° and proved to be 1-cyanohydrocotarnine (VI) (according to the analytical data and mixed melting point).

Found %: N 11.33. $C_{13}H_{14}O_3N_2$. Calculated %: N 11.38.

1,3-Di-(1-hydrocotarnyl)acetone (III).

a) 4.74 g of cotarnine was dissolved in 20 ml of pyridine and mixed with 1.46 g of acetonedicarboxylic acid. After an hour's standing at room temperature the pyridine was distilled off in vacuo. After recrystallization of the residue from acetone 3.17 g (64%) was obtained of a compound with m. p. 162°, which gave no depression in melting point with the compound obtained by Dey and Kantam [2], also recrystallized from acetone.

b) 2.7 g of 1-hydrocotarnylacetone was dissolved by heating in 15 ml of 95% alcohol, then 0.05 g of anhydrous sodium carbonate and 2.37 g of cotarnine were added to the solution. The cotarnine dissolved almost instantaneously, forming a light red solution. After 12 hours' standing, copious crystallization began, ending after 2 days' standing in a refrigerator. After recrystallization of the crude product first from methyl alcohol, and then from acetone, 3.6 g (73%) of a compound with m. p. 162° was obtained.

Found %: C 65.31; H 6.31; N 5.73. M 517 (in benzene). Calculated %: C 65.30; H 6.50; N 5.64. M 496.55.

1-(5-Bromohydrocotarnyl) acetone (VII).

a) To 2.48 g of 1-hydrocotarnylacetone, dissolved by moderate heating in 20 ml of glacial acetic acid and cooled to room temperature, was added dropwise with vigorous stirring a solution of 0.52 ml of bromine in 5 ml of glacial acetic acid. In the places where the bromine touched the solution a precipitate immediately separated, which dissolved upon stirring. After all of the bromine had been added, an orange-colored solution was produced. After 3 hours' standing the solvent was distilled off in vacuo; the colored residue after trituration with 15 ml of anhydrous ethyl acetate was converted to a crystalline material. After separation and washing with anhydrous ethyl acetate, 3.47 g (89%) of a material was obtained that melted after recrystallization from alcohol at 162-163°.

Found %: N 3.50; Br^- 18.62. $C_{15}H_{18}O_4NBr \cdot HBr$. Calculated %: N 3.21; Br^- 18.28.

0.44 g of the hydrobromide of 1-(5-bromohydrocotarnyl)acetone was dissolved by moderate heating in 5 ml of water, then cooled and mixed with 1 ml of 10% sodium hydroxide. The oily precipitate that separated solidified in the course of several days. The yield amounted to 0.36 g of a substance that melted after recrystallization from acetone at 123-126°.

Found %: C 50.74; H 5.00. $C_{15}H_{18}O_4NBr$. Calculated %: C 50.57; H 5.09.

b) 2.22 g of 5-bromocotarnine was shaken with 10 ml of acetone and 0.5 ml of saturated sodium carbonate solution, then kept at room temperature for 2 days. After the acetone was distilled off, 30 ml of water was added to the residue; the tarry material that separated quickly crystallized. Yield 2.26 g. After recrystallization from light benzene or acetone a compound was obtained that melted at 125-126° and gave no depression in melting point with 1-(5-bromohydrocotarnyl)acetone obtained by method "a." After converting it to the hydrobromide a compound was obtained that melted at 162-163° (decomp.), and gave no depression in melting point with the hydrobromide obtained by method "a."

1,3-Di-(5-bromohydrocotarnyl)acetone (VIII). To a solution of 2.48 g of 1,3-di-(1-hydrocotarnyl)acetone in 20 ml of glacial acetic acid, obtained by moderate heating, after cooling and with vigorous stirring there was added dropwise 0.52 ml of bromine with glacial acetic acid. The clear solution obtained at the end of the addition was stirred for an hour more, then the solvent was distilled off in vacuo. The residue (5.32 g) was recrystallized from butanol; a product was obtained with m. p. 137° (decomp.)

Found %: N 3.75; Br^- 19.73. $C_{27}H_{30}O_7N_2Br_2 \cdot 2HBr$. Calculated %: N 3.44; Br^- 19.58.

1-Hydrocotarnylacetone methiodide (IX). 1.24 g of 1-hydrocotarnylacetone was dissolved in 7.5 ml of benzene, then 2.05 g of methyl iodide was added and all was boiled on a water bath for 1 hour. The benzene and methyl iodide were decanted from the tarry substance that had formed, and the residue was crystallized from alcohol. Yield 1.75 g (93%). White, crystalline material, melting at 145-147°.

Found %: C 45.51; H 5.49. $C_{16}H_{22}O_4NI$. Calculated %: C 45.83; H 5.29.

N-Methylcotarnylideneacetone methiodide (X). 1.24 g of 1-hydrocotarnylacetone was mixed with 5 ml of water and 0.9 ml of methyl iodide, whereupon the mixture boiled up. A solid, crystalline substance separated, to which were added 0.2 g of NaOH dissolved in 1 ml of water, and 0.5 ml of methyl iodide. The mixture was heated on a water bath for 1 hour. The yellow, crystalline product that was obtained was separated off, washed with water, then recrystallized from methyl alcohol. Yield 1.6 g (83%). M. p. 203-204°.

Found %: C 46.75; H 5.32. $C_{17}H_{24}O_4NI$. Calculated %: C 47.12; H 5.46.

1,3-Di-(1-hydrocotarnyl)acetone bis-methiodide (XI). 1.24 g of 1,3-di-(1-hydrocotarnyl)acetone was dissolved in 20 ml of benzene, mixed with 0.75 ml of methyl iodide, and left at room temperature for 2 hours. The crystals (0.85 g) that separated melted after recrystallization from alcohol at 228°. After 2 days' standing another 1.15 g of the methylated product was separated from the reaction mixture, which was purified with much more difficulty than the initial material.

Found %: C 44.45; H 4.59. $C_{29}H_{38}O_7N_2I_2$. Calculated %: C 44.63; H 4.91.

N,N'-Dimethyldicotarnylideneacetone bis-methiodide (XII). 1.24 g of 1,3-di-(1-hydrocotarnyl)acetone suspended in 10 ml of water was mixed with 0.75 ml of methyl iodide and a solution of 0.20 g of NaOH in 1 ml of water, after which the mixture was heated on a water bath for 1 hour. The crystals that precipitated were separated out on the following day and washed with water. Yield 1.83 g (87%). The compound, which was recrystallized from alcohol, started to darken at 260°, but did not melt upon heating to 280°.

Found %: C 44.08; H 5.49; N 3.08. $C_{31}H_{42}O_7N_2I_2 \cdot 2H_2O$. Calculated %: C 44.08; H 5.45; N 3.32.

In conclusion, we than G. Zemplen, I. Batta, K. Shimon-Orman, Yu. Varshani, I. Plive, Yu. Vadas and Yu. Knirsh for their assistance and interest.

SUMMARY

It has been shown that the products of the condensation of cotarnine with acetone are not ring-chain tautomers, as was suggested previously, but that both of these compounds have a cyclic structure. The compound melting at 83° is 1-hydrocotarnylacetone, and the compound with m. p. 162-163° is 1,3-di-(1-hydrocotarnyl) acetone.

Thus, it has been possible to disprove the assertion concerning the ring-chain tautomerism of cotarnine and its derivatives, and to make superfluous the assumption of the existence of an aminoaldehyde form of cotarnine.

LITERATURE CITED

[1] C. Lieberman, F. Kropf, Ber. 37, 211 (1904).

[2] B. B. Dey, P. L. Kantam, J. Indian Chem. Soc. 12, 430 (1935).

[3] W. J. Gensler, R. C. Elderfield, Heterocyclic Compounds 4, 465 (1952).

[4] V. A. Maslennikova and G. V. Lazuryevsky, Proc. Acad. Sci. USSR, 72, 305 (1950).

[5] D. Beke, K. Kharshani and I. Kereshi, J. Gen. Chem. 27, 2760 (1957).*

[6] D. Beke and M. Martosh-bartsai, J. Gen. Chem. 27, 1836 (1957).*

[7] D. Beke and K. Kharshani, J. Gen. Chem. 27, 2108 (1957). *

[8] C. K. Ingold, Structure and Mechanism in Organic Chemistry, 580 (1953).

Received March 3, 1956

Budapest Polytechnic University

*Original Russian pagination. See C. B. Translation.

REACTIONS OF FREE RADICALS IN SOLUTIONS

XIII. STUDY OF THE MECHANISM OF THE INHIBITING EFFECT OF QUINONES ON THE INITIATION OF POLYMERIZATION

B. A. Dolgoplosk and G. A. Parfenova

A number of investigations have been devoted to the inhibiting effect of quinones on the process of polymerization.

Some authors note that the presence of benzoquinone, duroquinone, and chloranil causes the appearance of induction periods in the polymerization of styrene and vinyl acetate under the influence of peroxide [1, 2]. Other authors [3] arrive at the conclusion that the effect of benzoquinone is different in principle in initiated and thermal polymerization processes, connecting the character of the action of the quinones with the nature of the primary active center. It is noted that complete inhibition of the process by the quinones is observed only in the case of the biradical nature of the primary active centers, i.e., in processes of thermal and photopolymerization. In processes of initiated polymerization, where usually the primary active centers are monoradical in nature, benzoquinone does not cause complete inhibition, but only reduces the rate of the process. These views also are reflected in recent work [4].

The present investigation has been devoted to a study of the mechanism of the inhibiting effect of benzoquinone in processes of initiated polymerization and to a study of the reaction of benzoquinone with free radicals.

DISCUSSION OF RESULTS

a). Effect of Quinones on the Kinetics of Polymerization

Unlike the peroxides and diazoamino compounds, the kinetics of the dissociation of the dinitrile of azoisobutyric acid in hydrocarbon solutions does not depend on the nature of the solvent or the presence in the system of one or another ingredient.

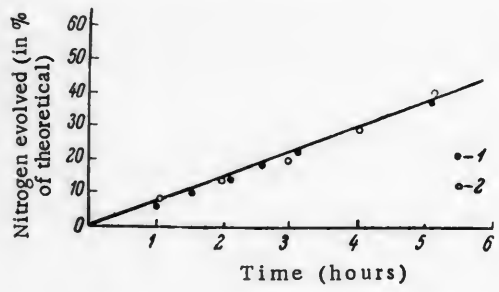


Fig. 1. Kinetics of thermal dissociation of the dinitrile of azoisobutyric acid in ethylbenzene solution at 70°.
Content of dinitrile 0.111 M, benzoquinone 0.222 M, 1) without quinone, 2) with quinone.

A study of the kinetics of the decomposition of the dinitrile of azoisobutyric acid in ethylbenzene solution at 70° has shown that the presence of benzoquinone does not exert any effect on the rate of evolution of nitrogen. From this it follows that the effect of the quinone in the case of the initiation of polymerization by the azodinitrile can be related only to its reaction with free radicals.

In the polymerization of styrene by the agency of the dinitrile of azoisobutyric acid, benzoquinone completely inhibits the process, causing the appearance of a definite induction period (Fig. 2).

The duration of the induction period at a given temperature is proportional to the concentration of the benzoquinone. The magnitude of the amount of the latter, when the molar ratio between the initiator and quinone is preserved, does not affect the extent of the induction period.

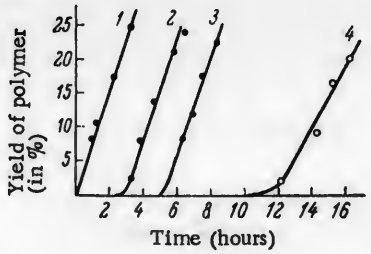


Fig. 2. Kinetics of polymerization of styrene in the presence of the dinitrile of azoisobutyric acid and different amounts of quinone at 60°.

Molar ratio $\frac{\text{quinone}}{\text{initiator}}$:1) without quinone;
2) 0.15, 3) 0.25, 4) 0.50.

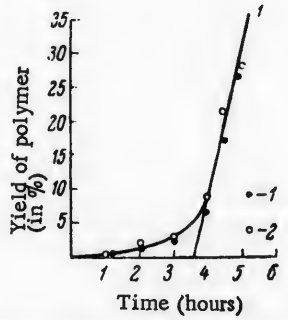


Fig. 3. Relationship of kinetics of polymerization of styrene to concentration of quinone with constant molar ratio $\frac{\text{quinone}}{\text{dinitrile}} = 0.5$.
Quinone content: 1) 0.0023 mole;
2) 0.0046 mole.

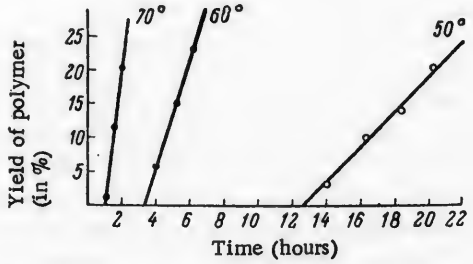


Fig. 4. Kinetics of polymerization of styrene in the presence of the dinitrile of azoisobutyric acid and benzoquinone at different temperatures.

Molar ratio $\frac{\text{quinone}}{\text{dinitrile}} = 0.15$.

The relationships established, resulting from the monomolecular mechanism of the thermal dissociation of the azodinitrile, are dependent upon the reaction of the benzoquinone with free radicals formed by the dissociation of the initiator. The beginning of the polymerization corresponds to the complete disappearance of the benzoquinone from the system.

An increase in the temperature of the process, causing an acceleration in the dissociation of the initiator, results in a shortening of the induction periods.

The activation energy of the process, calculated from the kinetics of the polymerization at different temperatures, is equal to 21.4 Cal.

The initiating effect of methylphenyltriazene is connected with its ability to dissociate upon heating in organic solvents with the formation of free radicals according to the following scheme [6]:

$$CH_3N{=}N{-}NHC_6H_5 \rightarrow CH_3^{\cdot} + C_6H_5NH^{\cdot} + N_2$$

In Fig. 5 and 6 the experimental data are given for the kinetics of the polymerization of styrene under the influence of methylphenyltriazene at different temperatures and in the presence of different amounts of benzoquinone.

The concentration of the initiator in both cases was 0.067 M.

From the information presented it follows that benzoquinone causes the appearance of a lengthy induction period, the duration of which is inversely related to the temperature of the process. The absence in the case in question of a proportional relationship between the concentration of the quinone and the duration of the induction period is connected, apparently, with the molecular reaction of the quinone with the triazene. This is confirmed by the fact that benzoquinone rather strongly accelerates the dissociation of methylphenyltriazene.

In the absence of benzoquinone the yield of gas is about 140% of the theoretical amount of nitrogen. The excessive amount (compared to the theoretical) of gas is dependent on the formation of methane in the reaction [6]: $CH_3^{\bullet} + RH \rightarrow CH_4 + R^{\bullet}$.

In the presence of benzoquinone the yield of gas is only 50% and contains practically no methane. The absence of the latter is directly related to the "catching" of the methyl radicals by the benzoquinone. The decrease in the yield of nitrogen is evidence that the reaction of benzoquinone with methylphenyltriazene is accompanied by the entrance of the azo group into the reaction products. Even when the triazene is mixed with benzoquinone in the solid state at room temperature, a blackening of the material

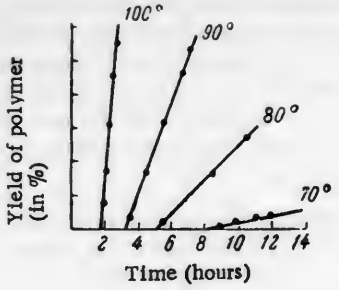


Fig. 5. Kinetics of polymerization of styrene in the presence of methylphenyltriazene and benzoquinone at different temperatures.

Molar ratio $\frac{\text{quinone}}{\text{initiator}} = 0.25$.

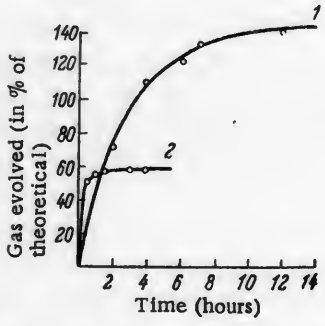


Fig. 7. Kinetics of decomposition of methylphenyltriazene in the presence of quinone at 100°.

Concentration of triazene 0.38 M, quinone 0.75 M.

1) Without quinone; 2) with quinone.

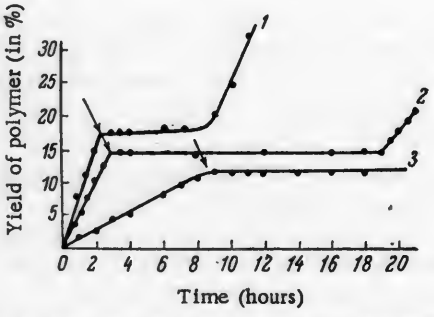


Fig. 9. Interruption of polymerization process by quinone at 60°.

1) Dinitrile of azoisobutyric acid; 2) benzoyl peroxide, 3) hydroperoxide of diisopropylbenzene. Moment of addition of quinone indicated by arrows.

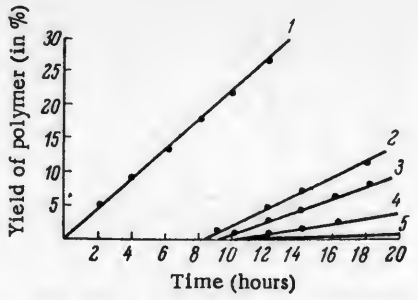


Fig. 6. Kinetics of polymerization of styrene in the presence of methylphenyltriazene at different quinone concentrations at 70°.

Molar ratio $\frac{\text{quinone}}{\text{triazene}}$: 1) without quinone; 2) 0.15; 3) 0.25; 4) 0.50; 5) 1.00.

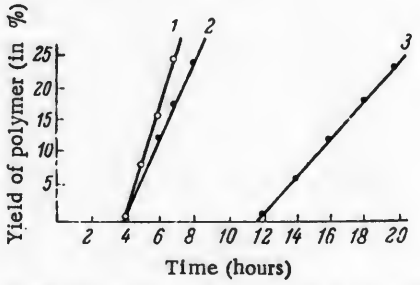


Fig. 8. Polymerization of styrene in the presence of benzoquinone under the influence of different initiators.

Molar ratio $\frac{\text{quinone}}{\text{initiator}} = 0.25$.

1) Benzoyl peroxide at 70°; 2) hydrogen peroxide of isopropylbenzene at 80°; 3) diazoaminobenzene at 100°.

is observed, which is connected with the formation of reaction products of a complex character.

In the case of the initiation of polymerization by diazoaminobenzene, benzoyl peroxide, or hydrogen peroxide of isopropylbenzene, benzoquinone exerts a similar inhibiting effect, causing an induction period, the duration of which is determined by the concentration of the inhibitor.

The inhibiting effect also appears in full measure upon introducing benzoquinone into the system at a given stage of the polymerization. In this case, the slower the polymerization process is initiated, the longer the induction period.

A study of the effect of some other quinones on the polymerization of styrene initiated by the dinitrile of azoisobutyric acid showed that naphthoquinone and

phenanthraquinone exert an inhibiting action, the effectiveness of the naphthoquinone being less than that of benzoquinone. Anthraquinone does not show any inhibiting effect. In the same way it was established that the character of the effect of different quinones on the initiated and thermal [5] polymerization processes is exactly the same.

b). Investigation of the Mechanism of the Reaction of Benzoquinone with Free Radicals

In this section the results are presented of our earlier work [6, 7] in an investigation of the composition of the products formed in the reaction of benzoquinone with the dimethylcyanomethyl radical.

1. Experiment demonstrating the ability of benzoquinone to "catch" free radicals. In this instance we utilized as a source of free radicals methylphenyltriazene, which breaks down at a temperature of 100° with the formation of nitrogen and free radicals that react with the solvents.

$$C_6H_5NH—N=NCH_3 \rightarrow CH_3\cdot + N_2 + C_6H_5NH\cdot$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot$$

The yield of methane when the triazene dissociates in benzene amounts to 39%. When the triazene decomposes under those same conditions, but in the presence of benzoquinone or naphthoquinone, methane is practically not detected in the gas (Table 1).

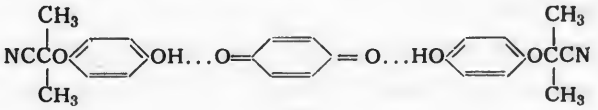
TABLE 1

Methane Content of Gas in Thermal Dissociation of Methylphenyltriazene in Ethylbenzene Solution
(temperature 100°, concentration of triazene 0.38 M)

Composition	Molar ratio $\frac{\text{quinone}}{\text{triazene}}$	Methane content of gas (in %)
Methylphenyltriazene	Without quinone	28.4
		29.0
		28.3
Methylphenyltriazene + benzoquinone	2.00	1.1
	1.95	1.6
	1.97	1.1
	1.97	0.0
	1.96	0.0
Methylphenyltriazene + naphthoquinone	1.97	1.5

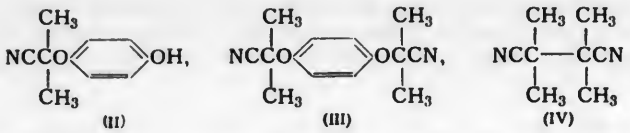
2. Products of reaction of benzoquinone with free radicals. As a source of free radicals we chose the dinitrile of azoisobutyric acid, which upon dissociation forms two identical radicals containing the nitrile group. The presence of the latter greatly facilitates the task of identifying the products.

1.5 mole of benzoquinone and 1 mole of the dinitrile of azoisobutyric acid in benzene solution were heated to boiling. The reaction was considered completed after the evolution of gas ceased, which indicated complete decomposition of the azodinitrile. Analysis of the decomposition products obtained showed the absence of hydroquinone in them. From the reaction mass we obtained the quinhydrone (I), consisting of two molecules of the ether of the hydroquinone and one molecule of benzoquinone.



(I)

After decomposition of the latter compound we isolated in pure form the monoether of the hydroquinone (II). Besides this, the diether of the hydroquinone (III) and the dinitrile of tetramethylsuccinic acid (IV) were identified among the products.



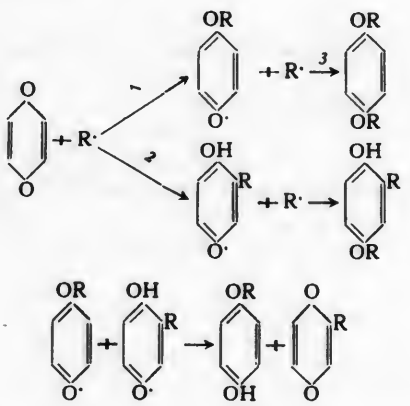
(II) (III) (IV)

In Table 2 are presented the data from two experiments on the yields of the products mentioned that were isolated in pure form and identified.

TABLE 2

Names of products isolated	Combination of free radicals (in % of theoretical)	
	experiment 1	experiment 2
Monoether of hydroquinone	19.0	14.5
Diether of hydroquinone	40.7	37.0
Dinitrile of tetramethylsuccinic acid	0.3	0.5
Residue and loss	40.0	48.0

On the basis of the products obtained, the following mechanism is presented for the reaction between the free radicals investigated and benzoquinone.



Direction 1 leads to rupture of the C=O bond, direction 2 to alkylation of the ring. Both directions of reaction are energetically very advantageous, since they lead to stable semiquinoid radicals. The inhibiting action of the quinones in the chain radical processes is connected with the formation of stable semiquinoid radicals incapable of participating in further development of the process.

EXPERIMENTAL

The loading of the monomers, the initiators, and the inhibitors into the ampoules, and also the polymerization process, were carried out under conditions that practically excluded the entrance of air.

Analyses of compounds isolated. The quinhydrone, consisting of the monomether of hydroquinone and benzoquinone (I), formed reddish-brown crystals with m. p. 97-98°. They precipitated from the reaction mass after part of the benzene was distilled off, upon cooling.

The benzoquinone content, determined by iodometric titration, was 23.6-26.7%, calculated 23.4%.

The hydroxyl group content was determined by the Tserevitinov-Chugaev method, and nitrogen by the Dumas method.

Found %: OH 8.2, 8.5; N 6.2, 6.0. $C_{26}H_{26}O_6N_2$. Calculated %: OH 7.2; N 6.1.

To break down the quinhydrone and remove the benzoquinone from it to a benzene solution, potassium iodide and hydrochloric acid were added to quantitatively convert the quinone to hydroquinone. The hydroquinone formed dissolved completely in water and the monoether that was freed remained in benzene solution, which was removed in vacuo. The monoether (II) was isolated as crystals with m. p. 51.5°.

Found %: C 67.9, 67.4; H 7.0, 6.7; N 7.7, 7.9; OH 9.8, 10.5. M 172, 187. $C_{10}H_{11}O_2N$. Calculated %: C 67.8; H 6.2; N 7.9; OH 9.6. M 177.

Separation of the diether of hydroquinone (III) was carried out by supplementary removal of the benzene by distillation in vacuo. Upon cooling the residual mass to minus 20-30°, crystals of the diether of the hydroquinone with m. p. 128-129° precipitated.

Found %: C 68.9; H 6.9; N 11.4, 11.5. M 246, 244. $C_{14}H_{16}O_2N_2$. Calculated %: C 68.8; H 6.6; N 11.5. M 244.

Along with the diether, trifling amounts of the dinitrile of tetramethylsuccinic acid (IV) with m. p. 168.5° were isolated by fractional crystallization.

Found %: C 70.7; H 8.9; N 20.6. $C_{18}H_{12}N_2$. Calculated %: C 70.6; H 8.8; N 20.7.

SUMMARY

1. The effect of benzoquinone on the kinetics of the initiated polymerization of styrene has been investigated.

It has been shown that independent of the nature of the initiator the quinones caused the appearance of an induction period, the duration of which is inversely related to the rate of formation of the initial active centers.

2. Under model conditions, the composition of the products of the reaction of benzoquinone with free radicals has been studied, and on the basis of the experimental data obtained a mechanism has been considered for the inhibiting action of quinones on chain radical processes.

LITERATURE CITED

[1] S. A. Cohen, J. Am. Chem. Soc. 69, 5, 1057 (1947).

[2] P. D. Bartlett, G. S. Hammond, Disc. of Farad. Soc., London 2, 242 (1947).

[3] H. W. Melville, W. F. Watson, Trans. Farad. Soc. 44, 886 (1948).

[4] A. F. Bickel, W. A. Waters, J. Chem. Soc. 1950, 1764.

[5] D. S. Korotkina, Diss.: "Investigation of the mechanism of the inhibiting action of polyphenols, aromatic amines and quinones on the process of thermal polymerization," (1950).

[6] G. A. Parfenova, Diss.: "Investigation of the mechanism of the inhibiting action of polyphenols, aromatic amines and quinones on the process of initiated polymerization," (1952).

[7] B. A. Dolgoplosk, D. S. Korotkina, G. A. Parfenova, B. L. Erusalimsky and E. B. Milovskaya, Problems of Chemical Kinetics, Catalysis and Reactivity, Acad. Sci. USSR Press, (1955).

Received October 22, 1956

INVESTIGATION OF THE SULFONATION REACTIONS

XLIII. SULFONATION OF BENZENE TO DISULFONIC ACIDS

A. A. Spryskov and S. P. Starkov

All the investigations known in the literature on the sulfonation of benzene to disulfonic acids can be divided into three groups.

To the first group belong the works published before 1910 [1]. Their special characteristic is the use of inadequate methods of analysis of the sulfo mixtures and the absence of data on the concentration of the sulfonating agent, the temperature, and other reaction conditions; therefore, very contradictory results were obtained on the p-benzenedisulfonic acid content of the mixture.

To the second group belong the investigations based on more adequate analytical methods. Holleman and Polak [2] used a thermal method of analysis for the m- and p-benzenedisulfonyl chlorides that were formed. Sulfonating barium benzenesulfonate at 183, 209, and 233° with 98% sulfuric acid, they found that with an increase in the temperature and the duration of the sulfonation, the amount of p-disulfonic acid rose from 10 to 23%; when 12.5% oleum was used, there was from 2 to 6% of the para-isomer formed.

Behrend and Mertelsmann [3] sulfonated benzene by passing it in vapor form through sulfuric acid heated to 240-250° in the presence of mercury, which catalyzed the conversion reaction of the isomers. Thus they obtained a sulfo mixture that contained 34% para-isomer. The determination of the isomers was carried out by mechanically separating the crystals of the m- and p-benzenesulfonyl chlorides after fractional crystallization of the sulfonates.

Mohrman [4] tested other metals besides mercury as catalysts for the isomerization of the benzenedisulfonic acids.

The methods of determining the isomers used by the authors of the works of the second group could give correct results only in the absence of mono- and trisulfonic acids of benzene in the mixture.

In the third group of investigations the goal was pursued of preparing m-benzenedisulfonic acid with a minimum expenditure of sulfuric acid. Thus, Rut [5] carried out monosulfonation with the monohydrate, and disulfonation with oleum, blowing air through the reaction mixture at the end of the exposure. Kamensky-Shmidt [6], and also Geiser and Korovitskaya [7] sulfonated benzene with sulfuric acid to the disulfonic acid using vacuum and catalysts at temperatures from 195 to 275°. They did not determine the para-isomer content. Shestov [8], studying the action of oleum on benzene, established that the formation of the disulfonic acids when using 60% oleum was completed in 3 hours at 70°. Along with the disulfonic acid the action of the oleum led to the formation of considerable amounts of the 3,3'-disulfonic acid of diphenyl sulfone, which he isolated and identified as the sulfonyl chloride with m.p. 180.6°. Fierz-David and Stamm [9] sulfonated benzene first with 20% and then with 66% oleum at 90°. The use of sulfur trioxide also has been investigated [10].

Thus, there is no description in the literature of sulfonation with the monohydrate over a wide temperature range with complete analysis of the sulfo mixture. There are no data on the effect of stirring, reaction temperature, or order of addition of the components when sulfonating with oleum. There are even contradictory results among the investigators of the second group.

The objective of the present work was the systematic study of the disulfonation of benzene.

EXPERIMENTAL

Sulfonation of benzene with monohydrate. The sulfonation experiments were set up in the following manner. To a weighed portion of frozen benzene in a test tube was added 6 moles of 100% sulfuric acid

TABLE 1

Sulfonation of Benzene With Monohydrate (6 moles per mole of benzene)

Expt. No's.	Period of heating (in hours)	Temperature	Found (in percent of total sulfonic acids)			
			monosulfonic acid	m-disulfonic acid	p-disulfonic acid	trisulfonic acid
1	10	115°	88.4	11.2	0.4	
2	2	150	49.9	47.4	2.7	
3	10	150	32.1	64.2	3.7	
4	2	178	32.5	60.9	6.6	
5	10	178	7.1	82.5	10.4	
6	2	206		89.8	10.2	
7	10	206		87.9	12.1	
8 *	10	208		88.1	11.9	
9	1	228	3.7	84.9	11.4	
10	10	228		83.8	16.2	
11 **	10	252		80.3	13.6	6.1

* Sulfonation in the presence of sodium sulfate. ** Anhydrous m-benzenedisulfonic acid was sulfonated with 4 moles of the monohydrate.

TABLE 2

Sulfonation of Benzene with 25% Oleum (2.5 moles of SO_3 per mole of benzene)

Period of heating (in hours)	Temperature	Found (in percent of total sulfonic acids)			
		m-disulfonic acid	p-disulfonic acid	diphenyl sulfone 3,3'-disulfonic acid	
				by direct method	by indirect method
10	96°	80.1	4.4	14.6	15.5
10	119	83.5	3.6	13.9	12.9
2	150	83.9	3.0	11.8	13.1

TABLE 3

Sulfonation of Benzene with 60% Oleum Without Stirring

Expt. No.	Temperature	Period of heating (in hours)	Found (in percent of total sulfonic acids)			
			m-acid	p-acid	diphenyl sulfone 3,3'-disulfonic acid	
					by direct method	by indirect method
1	96°	10	73.2		26.8	25.5
2	90	10	71.2	0.9	28.9	27.9
3	120	10	69.0	1.2	29.3	29.8
4	145	10	70.1	0.9	29.6	29.0
5	150	2	66.1	1.3	30.6	29.6

(monohydrate) per mole of benzene. The test tube, after being sealed, was shaken until the benzene dissolved completely and was heated in an Eikman apparatus. The sulfo mixture was analyzed for the mono- and disulfonic acid content or the di- and trisulfonic acid content by the method of Kiprianov and Sych [11]. The quantity of para-isomer was determined with benzidine [12]. Tests with phenylhydrazine solution [12] showed that the ortho-isomer was absent in all the sulfo mixtures.

TABLE 4

Sulfonation of Benzene with 60% Oleum with Stirring and Holding at 90° for 3 Hours (2.5 moles of free SO_3 per mole of benzene)

Experiment No.	Found (in percent of total sulfonic acids)			Remarks
	para-isomer	diphenyl sulfone 3,3'-disulfonic acid		
		by direct method	by indirect method	
1		18.9	17.9	In oleum, 2.75 moles of SO_3 per mole of benzene introduced.
2		19.8	19.1	Stirrer made 60 revolutions per minute.
3		18.8	18.2	With more vigorous stirring while holding.
4	1.2	17.2	16.7	Very vigorous stirring.
5		22.3	22.5	The mixture was not stirred while holding
6		29.4		Oleum was introduced into the benzene

TABLE 5

Sulfonation of Benzene with 20 and 65% Oleum in two Stages

Found (in percent of total sulfonic acids)			Remarks
para-isomer	diphenyl sulfone 3,3'-disulfonic acid		
	by direct method	by indirect method	
—	12.5	13.4	Stirring at 60 revolutions per minute.
1.2	10.5	9.5	Stirrer made about 600 revolutions per minute
—	10.4	—	

TABLE 6

Determination of the Chloride of Diphenyl Sulfone 3,3'-Disulfonic Acid in Mixtures with m-Benzenedisulfonyl Chloride

Chloride used			Chloride of sulfone disulfonic acid found (in %)	Error (in %)	Melting point of chloride	Ligroin used (ml)
m-disulfonic acid (in %)	sulfone disulfonic acid (in %)	total weight (g)				
74.8	25.2	0.5046	24.6	—0.6	174—176°	70
89.8	10.2	0.5030	9.5	—0.7	174—176	70
89.8	10.2	1.0004	10.2	0	173—176	120
97.5	2.5	2.000	2.4	—0.1	173—176	220

The results of the experiments presented in Table 1 show that the formation of benzenedisulfonic acids practically starts a little below 115° with a concentration of sulfuric acid in the mixture of about 96.5%. The formation of disulfonic acids is completed in 2 hours at 206° with a concentration of 91.5% of sulfuric acid in the mixture. The formation of trisulfonic acid at a slow rate is possible only at 250° or a little lower, as was shown by the results of the last experiment in Table 1, in which anhydrous m-benzenedisulfonic acid was sulfonated. The para-isomer was formed as a result of isomerization of the meta-acid. The results of experiment 8 showed that the presence in the mixture of sodium sulfate does not change the composition of the sulfo mixture.

At the sulfonation temperature of the first five experiments in order, the disulfonic acids formed still could not be hydrolyzed [13] and the p-benzenedisulfonic acid therefore was obtained in these experiments only by direct sulfonation of the monosulfonic acid. Since the para-isomer is the most stable isomer, its rate of formation increases with a rise in temperature. In benzenesulfonic acid the electron density in the para-position to the sulfo group is less than in the meta-position [14]. Consequently the meta-isomer is predominantly formed by the action of an electrophilic reagent, since the substitution reaction proceeds in the meta-position with a lesser activation energy than in the para-position. With an elevation in temperature there is an increase in the number of active molecules capable of overcoming the higher energy barrier to substition in the para-position, as a result of which the para-isomer content increases. Actually, at 115° the amount of para-isomer comprises 3.5% of the total disulfonic acids, at 150° 5.5%, and at 178° 10-11%. At higher temperatures p-benzenedisulfonic acid is formed both by direct sulfonation of the mono-acid and as a result of isomerization of the m-disulfo-isomer.

Steric factors hinder the formation of o-benzenedisulfonic acid. According to contemporary ideas, the sulfonating form may be the cation HSO_3^+ or the cation $H_3SO_4^+$ [15]. Both of these are of considerable size. In particular the latter, which is the most probable sulfonating form, has a tetrahedral structure. Its entrance into the ortho-position to a sulfo group existing in the ring is so much hindered that formation of the ortho-isomer is practically imperceptible.

In the reaction mixture of experiment 6, 1% of the 3,3'-disulfonic acid of diphenyl sulfone was found by the direct method described below.

Sulfonation of benzene with 25% oleum. The experiments were carried out in the same manner as in the sulfonation with the monohydrate. For 1 mole of benzene an amount of oleum was introduced that contained 2.5 moles of free SO_3. The amount of diphenyl sulfone 3,3'-disulfonic acid in the sulfo mixture was determined by the direct method (see below) and by the indirect method of Kiprianov and Sych [11], described for the determination of benzene mono- and disulfonic acids; the paraisomer was determined through the benzidine salt [12].

The results of the experiments presented in Table 2 show that the amount of diphenyl sulfone 3,3'-disulfonic acid in the sulfo mixture is greatly increased in comparison with the experiments on sulfonation with the monohydrate. Disulfonation with oleum starts considerably below 100°, and consequently when 150° is reached, the disulfonation process is already vigorously under way. Thus, the disulfonation of benzene with 25% oleum, proceeding at a lower temperature in comparison with the sulfonation with the monohydrate, yields a sulfo mixture with a small para-isomer content, but with a considerable amount of diphenyl sulfone 3,3'-disulfonic acid.

Sulfonation of benzene with 60% oleum. To a weighed amount of oleum cooled below 0° in a test tube, benzene was added and cooled until solidification occurred. Then the test tube was sealed, carefully shaken until the benzene dissolved, and heated without mixing. The paraisomer content in the sulfo mixture was determined by the benzidine method, and diphenyl sulfone 3,3'-disulfonic acid by the direct and indirect methods. The results of the experiments, given in Table 3, show that the diphenyl sulfone 3,3'-disulfonic acid content does not depend on the temperature of sulfonation and amounts to 29% of the total sulfonic acids. The p-benzenedisulfonic acid content in all experiments was about 1%. In experiment 1 the sealed test tube with the mixture was rapidly rotated while heating for the purpose of mixing, which led to a lowering of the diphenyl sulfone 3,3'-disulfonic acid content; therefore the experiments were executed with mixing.

In a three-necked flask provided with a dropping funnel, a stirrer with a liquid seal, and a thermometer, benzene was added to 62% oleum at a temperature below 45° with stirring. After the benzene was run in, the mixture was heated at 90° for 1½ hours and was heated for 3 hours with continuous stirring at that temperature. The results given in Table 4 show that stirring greatly lowered the diphenyl sulfone 3,3' disulfonic acid content of the mixture. The vigor of stirring also had an effect on the composition of the mixture, as comparison of the results of experiments 2-4 shows. The

sulfone disulfonic acid content is decreased by 2.5%. A change in the order of addition of the reactants in experiment 6 (adding oleum to the benzene) resulted in a sharp increase in the sulfone disulfonic acid content.

One of the well known ways of preparing m-benzenedisulfonic acid is the sulfonation of benzene in two stages (see [9] et al.). First the benzene is introduced with stirring at 40-45° into 20% oleum, which contains 0.4 mole of free sulfur trioxide per mole of benzene. Then the mixture is heated in the course of 1.5 hours to 90°, held for 1 hour, cooled, and at a temperature not higher than 75°, 60% oleum is added, containing 2.2 moles of free SO_3 per mole of benzene. The mixture is held at 90° for 3 hours. The results of the experiments, given in Table 5, showed that a significant increase in the vigor of stirring also lowered the diphenyl sulfone 3,3'-disulfonic acid content by 2.5-3%.

In the last experiment the mixture was kept in the monosulfonation stage at 120°.

Finally, the previously suggested [16] sulfonation of benzene sulfonic acid with 65% oleum was tried. To benzenesulfonic acid containing 3.3% water there was added dropwise, with stirring at 30-40°, 65% oleum containing 1.5 moles of free SO_3 per mole of sulfonic acid. The mixture was heated during the course of 2 hours to 90° and held for 3 hours at this temperature. In the sulfo mixture obtained there was found by the direct method 7.7% of the sulfone disulfonic acid.

Evaluating the results of all the experiments that have been described, we can conclude that of all the methods of preparing m-benzenedisulfonic acid, which is further transformable into resorcinol, the most practical and efficient method is the sulfonation with 60-65% oleum of the sulfonated mixture obtained by "vapor phase" sulfonation of benzene to the monosulfonic acid. The mixture obtained in this way contains less excess sulfuric acid than the sulfo mixtures obtained by other methods. In this way there are obtained about 1% of the para-isomer (of the total disulfonic acids) and 7-8% of diphenyl sulfone 3,3'-disulfonic acid, which yields 1 mole of resorcinol upon alkali fusion [17].

Determination of diphenyl sulfone 3,3'-disulfonic acid by the direct method consisted in separating the sulfuric acid as barium sulfate. The sodium salts of the sulfonic acids were converted into a mixture of sulfonyl chlorides, 0.7 g of which was treated for 1 hour in a shaker at room temperature with 100 ml of ligroin (fraction boiling up to 100°), saturated with the chloride of diphenyl sulfone, 3,3'-disulfonic acid. The chloride of the m-disulfonic acid dissolved during this treatment, and that of sulfone disulfonic acid was filtered off and weighed. The results of a test of this method, which is well known in principle [8], on synthetically prepared mixtures of the pure chlorides are given in Table 6.

SUMMARY

1. When benzene was sulfonated with 6 moles of monohydrate, it was found that disulfonation practically begins somewhat below 115°, and trisulfonation somewhat below 250°. With an increase in the sulfonation temperature the amount of p-benzenedisulfonic acid increases from 3.5 to 11% of the total disulfonic acids; about 1% of diphenyl sulfone 3,3'-disulfonic acid is formed.

2. Sulfonation of benzene with 25% oleum yields about 4% of the paraisomer and 12-15% of the sulfone 3,3'-disulfonic acid.

3. Upon sulfonation with 60% oleum without stirring, the amount of para-isomer falls to 1%, and the sulfone disulfonic acid increases to 29%. Stirring during sulfonation lowers the amount of the latter to 17% of the total disulfonic acids.

4. By two-stage sulfonation with 20 and 65% oleum, it is possible to obtain a sulfo mixture containing 1% para-isomer and about 10% diphenylsulfone disulfonic acid.

5. The most practically efficient method is the sulfonation with 65% oleum of the sulfo mixture obtained by "vapor phase" sulfonation of benzene to the monosulfonic acid. Thus, the sulfo mixture obtained contains 1% para-isomer, 7-8% sulfone disulfonic acid, and less excess sulfuric acid than the sulfo mixtures obtained by other methods.

6. o-Benzenedisulfonic acid was absent from all the sulfo mixtures.

LITERATURE CITED

[1] L. Barth, C. Senhofer, Ber. 8, 1477 (1875); V. Meyer, W. Michler, Ber. 8, 817 (1875); G. Heinzelmann, Ann. Chem. Pharm. 188, 157 (1877); J. Troger, W. Meine, J. pr. Ch. [2] 68, 314 (1903) and others.

[2] A. F. Holleman, J. J. Polak, Rec. trav. chim. 29, 416 (1910).

[3] R. Behrend, M. Mertelsmann, Lieb. Ann. 378, 352 (1911).

[4] G. Mohrman, Lieb. Ann. 410, 373 (1915).

[5] D. Rut, Anil.-Dye. Indus., 7, 12 (1932).

[6] I. N. Kamensky-Shmidt, Symp. Inst. Chem. Technol. Acad. Sci. URSR, 3, 21 (1937).

[7] G. K. Geiser and M. Ya. Korovitskaya, ibid., 9, 135 (1938).

[8] A. P. Shestov, J. Gen. Chem. 26, 1219 (1956).*

[9] H. E. Fierz-David, G. Stamm, Helv. Chim. Acta 25, 365 (1942).

[10] A. V. Topchiev and Ya. M. Paushkin, J. Phys. Chem. 12, 64 (1939); Amer. Pat. 1,999,955 (1935); Zbl. 1935, II 2126.

[11] A. I. Kiprianov and E. D. Sych, Factory Lab., 3, 623 (1934).

[12] A. A. Spryskov and S. P. Starkov, J. Gen. Chem. 26, 2607 (1956).*

[13] A. A. Spryskov and S. P. Starkov, J. Gen. Chem. 26, 2862 (1956).*

[14] A. A. Spryskov, J. Gen. Chem. 27, 1949 (1957).*

[15] W. A. Cowdrey, D. S. Davies, J. Chem. Soc. 1949, 1871; J. Brand, J. Chem. Soc. 1950, 1004; A. A. Spryskov, J. Gen. Chem. 25, 1733 (1955)*; B. I. Karavaev and A. A. Spryskov, J. Gen. Chem. 26, 503 (1956).*

[16] Brit. Pat. 683,439 (1952); Chem. Abs., 47, 3882 (1953).

[17] A. P. Shestov and N. A. Osipova, J. Gen. Chem. 26, 2005 (1956).*

Received October 12, 1956

Ivanovo Chemico-Technological Institute

* Original Russian pagination. See C. B. Translation.

HALOGENATION OF AROMATIC SILANES

V. PREPARATION AND PROPERTIES OF CHLOROBENZYL- AND CHLORO-p-TOLYLTRICHLOROSILANES CONTAINING CHLORINE ATOMS IN THE ALIPHATIC PART OF THE RADICAL

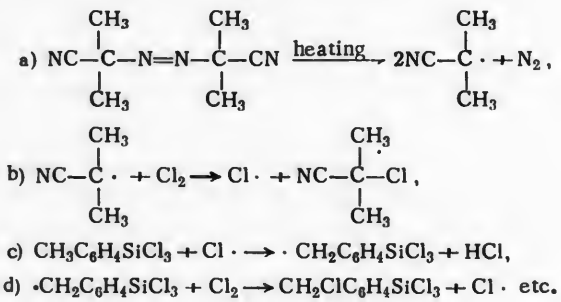
G. V. Motsarev and A. Ya. Yakubovich

We described earlier the preparation and properties of chloro derivatives of benzyltrichlorosilane and p-tolyltrichlorosilane, substituted in the aromatic nucleus [1]. These compounds were synthesized by chlorinating the silanes in the presence of the catalysts usually used in the halogenation of aromatic compounds (metallic iron, $SbCl_3$).

The purpose of this investigation was to study the possibility of preparing chlorobenzyl- and chloro-p-tolyltrichlorosilanes with chlorine atoms in the side chain, i.e., in the aliphatic part of the radical. There is no description in the literature of these compounds with the exception of α-chlorobenzyltrichlorosilane $C_6H_5CHClSiCl_3$ which was prepared by chlorinating benzyltrichlorosilane with sulfuryl chloride in the presence of benzoyl peroxide [2]. At the same time the preparation of halogen derivatives of aliphatic silanes are described in detail in the literature [3]. The methods known at the present time for preparing chloro derivatives of aliphatic silanes consist of the chlorination of these compounds either using elementary chlorine (in the presence of PCl_5 or ultraviolet radiation) in an organic solvent (CCl_4) or without it, or using sulfuryl chloride in the presence of benzoyl peroxide.

The last two cases of alkylsilane chlorination examined are chain processes, initiated either by light which causes the dissociation of molecular chlorine into atoms, or by benzoyl peroxide, which is capable of forming free radicals in the reaction. As is known, another such source of free radicals is isobutyric azodinitrile which has recently been widely used in practice in the chlorination of aliphatic and aliphatic-aromatic compounds [4]. Chlorination of organosilicon compounds in the presence of isobutyric azodinitrile is not described in the literature. In connection with this, it seemed interesting to check this chlorination method in the case we are examining, for preparing chloro derivatives of benzyl and p-tolyltrichlorosilanes with chlorine atoms in the aliphatic part of the radical.

It might be expected that chlorination of p-tolyltrichlorosilane (similarly to benzyltrichlorosilane) in the presence of isobutyric azodinitrile may proceed by a chain reaction



a) $NC-C(CH_3)_2-N=N-C(CH_3)_2-CN \xrightarrow{\text{heating}} 2NC-C(CH_3)_2\cdot + N_2$,

b) $NC-C(CH_3)_2\cdot + Cl_2 \rightarrow Cl\cdot + NC-C(CH_3)_2-Cl$,

c) $CH_3C_6H_4SiCl_3 + Cl\cdot \rightarrow \cdot CH_2C_6H_4SiCl_3 + HCl$,

d) $\cdot CH_2C_6H_4SiCl_3 + Cl_2 \rightarrow CH_2ClC_6H_4SiCl_3 + Cl\cdot$ etc.

and result in the formation of all possible substitution products in the methyl group. Actually, it was established experimentally that at 85-140°, with suitable molar ratios of silane and chlorine and using the catalyst indicated, the whole range of chloro-p-tolyltrichlorosilanes (from mono- to trichloro derivatives) may be obtained, containing the chlorine atoms in the methyl group, while in the case of benzyltrichlorosilane, α-chloro- and α,α'-dichlorobenzyltrichlorosilanes may be obtained in 83-90% yields. Chlorination of p-tolyltrichlorosilane and benzyltrichlorosilane in the side chain proceeded under these conditions quite smoothly without any signs of decomposition of the starting materials or reaction products, and the process may be readily controlled to form compounds with the required degree of substitution. As the catalyst was continually being consumed in the above reactions (see equation b), it had to be added periodically during the whole chlorination process as soon as the hydrogen chloride stopped being evolved. The total catalyst consumption was not greater than 0.7% of the weight of the starting silane.

All the chloro derivatives of p-tolyltrichlorosilane and benzyltrichlorosilane with chlorine atoms in the aliphatic part of the radical were separated individually and the physico-chemical characteristics of the p-mono-, di- and trichloromethyl derivatives of phenyltrichlorosilane and α,α'-dichlorobenzyltrichlorosilane are given for the first time.

Para-chloromethyl derivatives of phenyltrichlorosilane and chlorobenzyltrichlorosilanes, with the exception of p-trichloromethylphenyltrichlorosilane, are colorless, mobile liquids that fume in air. The trichloromethyl derivative is a white crystalline material (prisms) that fumes in air. The boiling points, densities and refractive indexes of these chloro derivatives increase with an increase in the chlorine content of the radical. They all have a sharp smell, distill without decomposition in vacuum, dissolve readily in organic solvents and on boiling with an alcohol solution of KOH (0.5 N), completely split out the chlorine, not only that which is bound to the Si atom, but also that in the aliphatic part of the radical (methyl group). These compounds are hydrolyzed at the Si—Cl bond when treated with water and form the corresponding polysilanes though no elimination of chlorine from the methyl group was observed under these conditions. Oxidation of these compounds with 20% nitric acid at 190-200° gave, in all cases, benzoic acid exclusively. The absence of chlorobenzoic acids in the oxidation products indicated that in chlorinating p-tolyltrichlorosilane and benzyltrichlorosilane in the presence of isobutyric azodinitrile, the substitution occurs exclusively in the aliphatic part of the radical and no chlorination of the aromatic nucleus takes place.

EXPERIMENTAL

Chlorination of p-tolyltrichlorosilane. Over a period of 4.5 hours, gaseous chlorine was passed at a rate of 20 ml/min. into a mixture of 14.3 g of p-tolyltrichlorosilane and catalyst, isobutyric dinitrile (0.1% of the weight of the silane). The chlorination was begun at 85° and then the temperature of the reaction mixture was gradually raised until it finally reached 130-140°. The catalyst was added at the beginning of the reaction and then several times during the whole course of the reaction as the rate of evolution of HCl slackened (not more than a total of 0.7% of the weight of silane). After flushing with dry air, the increase in weight of the reaction mixture was 6.2 g (compared with 6.5 g, required for chlorination to the trichloromethyl derivative). The chlorination product crystallized as it was cooled. Distillation in vacuum (14 mm) gave a fraction with b. p. 160-165°, 19.5 g. After a second distillation of the fraction, we obtained 18.2 g of a clear, colorless liquid with b. p. 162-163° at 14 mm, which crystallized on cooling to give long clear prisms of p-(trichloromethyl)-phenyltrichlorosilane. The yield was 90%, calculated on the p-tolyltrichlorosilane taken.

p-(Trichloromethyl)-phenyltrichlorosilane is a white crystalline substance, which fumes in air, forms prisms (from ether) and has b. p. 162-163° at 14 mm and m. p. 66-67°.

Found %: Cl (total*) 64.5, 64.9; Cl (hydrolyzable**) 32.0, 31.9. $C_7H_4Cl_6Si$. Calculated %: Cl (total) 64.74; Cl (hydrolyzable) 32.37.

Chlorination of p-tolyltrichlorosilane to mono- and dichloromethyl derivatives was carried out in a similar way under the same conditions; the amount of chlorine passed in was approximately decreased.

* The "total" chlorine was determined by Volhard's method, after boiling a sample of the silane with 0.5 N alcohol solution of KOH.

** The "hydrolyzable" chlorine was determined by Volhard's method after boiling a sample of the silane with water.

From 14.0 g of p-tolyltrichlorosilane, which was chlorinated for 1 hour 15 minutes (increase in weight 2.1 g), we obtained 13.8 g of a colorless liquid – p-(chloromethyl)-phenyltrichlorosilane. The yield was 85.7%, calculated on the p-tolyltrichlorosilane taken.

p-(Chloromethyl)-phenyltrichlorosilane is a colorless, mobile liquid, which fumes in air.

B. p. 142-144° at 15 mm, d_{20}^{20} 1.4078, n_D^{20} 1.5480.

Found %: Cl (total) 54.5, 54.6; Cl (hydrolyzable) 41.2, 41.1. $C_7H_6Cl_4Si$. Calculated %: Cl (total) 54.6; Cl (hydrolyzable) 40.96.

After chlorination for 2 hours 50 minutes (increase in weight 4.0 g), 14.5 g of p-tolyltrichlorosilane yielded 15.6 g of a colorless liquid, which fumed in air – p-(dichloromethyl)-phenyltrichlorosilane. The yield was 83.4%, calculated on the p-tolyltrichlorosilane taken.

p-(Dichloromethyl)-phenyltrichlorosilane is a colorless, oily liquid, which fumes in air.

B. p. 153-155° at 15 mm, d_{20}^{20} 1.4788, n_D^{20} 1.5541.

Found %: Cl (total) 60.1, 60.2; Cl (hydrolyzable) 36.7, 36.4. $C_7H_5Cl_5Si$. Calculated %: Cl (total) 60.27; Cl (hydrolyzable) 36.16.

The reaction products from the oxidation of p-(trichloromethyl)-phenyltrichlorosilane with 20% nitric acid at 190-200° yielded benzoic acid (yield 77%; m. p. 121°), which was identified by nitration with fuming HNO_3 to give m-nitrobenzoic acid with m. p. 141.5°. Similar results were obtained on oxidizing p-(chloromethyl)- and p-(dichloromethyl)-phenyltrichlorosilane.

Chlorination of benzyltrichlorosilane. Over a period of 1.5 hours, gaseous chlorine was passed at a rate of 20 ml/min. into a mixture of 18.1 g of benzyltrichlorosilane and catalyst – isobutyric dinitrile (added periodically during the whole course of the chlorination; the total amount was not more than 0.7% of the weight of the silane) – at 85-95°. After flushing with dry air, the increase in weight of the reaction mixture was 2.5 g (compared with 2.7 g, required for chlorination to the mono-α-chloro derivative). On distilling the chlorination product in vacuum (15 mm), we isolated 18.1 g of α-chlorobenzyltrichlorosilane. The yield was 87.0%, calculated on the benzyltrichlorosilane taken.

α-Chlorobenzyltrichlorosilane is a colorless, mobile liquid, fuming in air.

B. p. 140-142° at 15 mm, d_{20}^{20} 1.4239, n_D^{20} 1.5466.

Found %: Cl (total) 54.6, 54.9; Cl (hydrolyzable) 41.2, 41.3. $C_7H_6Cl_4Si$. Calculated %: Cl (total) 54.6; Cl (hydrolyzable) 40.96.

Chlorination of benzyltrichlorosilane to the α,α-dichloro derivative was carried out in a similar way, with an appropriate increase in the amount of chlorine passed in.

Chlorination of 19.2 g of benzyltrichlorosilane for 3.5 hours (at 85-125°) yielded 22.6 g of a colorless liquid, which was α,α,dichlorobenzyltrichlorosilane. The yield was 90%, calculated on the benzyltrichlorosilane taken.

α,α-Dichlorobenzyltrichlorosilane is a colorless, oily liquid, fuming in air.

B. p. 148-149° at 15 mm, d_{20}^{20} 1.4896, n_D^{20} 1.5557.

Found %: Cl (total) 60.3, 60.6. $C_7H_5Cl_5Si$. Calculated %: Cl (total) 60.27.

On oxidizing α,α-dichlorobenzyltrichlorosilane with 20% nitric acid at 190-200°, we obtained benzoic acid (yield 84%), m. p. 121.3°.

SUMMARY

1. Using p-tolyltrichlorosilane and benzyltrichlorosilane as examples, we established the possibility of chlorinating organosilicon compounds with elementary chlorine in the presence of isobutyric azodinitrile as catalyst, without breaking the Si–C bond, to give the whole range of chloro derivatives, containing chlorine atoms in the aliphatic part of the radical. No chlorination of the aromatic silane nucleus was observed under these conditions.

2. We isolated individually and characterized physico-chemically p-(chloromethyl)-, p-(dichloromethyl)- and p-(trichloromethyl)-phenyltrichlorosilanes, that have been unknown up to now, and α-α-dichlorobenzyltrichlorosilane.*

LITERATURE CITED

[1] G. V. Motsarev, A. Ya. Yakubovich, J. Gen. Chem. 26, 2622 (1956)** 27, 1318 (1957).**

[2] J. J. Bride, H. C. Beachell, J. Am. Chem. Soc. 70, 2532 (1948).

[3] K. A. Andrianov, Organosilicon Compounds,*** Moscow, State United Sci. Tech. Press, 121, 304-306 (1955); E. P. Mikheev, Proc. Acad. Sci. USSR, 108, 484 (1956).**

[4] A. V. Topchiev, B. A. Krentsel, Chem. Sci. and Ind. 1, 256 (1956); C. D. Nenitescu, Rev. Chim. 4, N 7-8 (1953).

[5] L. W. Frost, J. Am. Chem. Soc. 78, 3855 (1956).

Received September 29, 1956

* After finishing this investigation a paper by Frost [5] was published which describes the preparation of p-(trichloromethyl)-phenyltrichlorosilane by photochemical chlorination of p-tolyltrichlorosilane (8 hours at 65° and 18 hours at 95-100°). The yield of p-(trichloromethyl)-phenyltrichlorosilane was 96%, m. p. 67.5-68° (from ether).

** Original Russian pagination. See C. B. Translation

*** In Russian.

SULFONIC ACIDS OF SULFONES AS SIDE PRODUCTS IN SULFONATION PROCESSES

IV. INVESTIGATION OF THE POSSIBILITY OF POLAROGRAPHIC DETERMINATION OF SULFONIC ACIDS OF 4,4'-DIMETHYLDIPHENYL SULFONE, 4,4'-DICHLORODIPHENYL SULFONE AND 2,2'-DINAPHTHYL SULFONE

A. P. Shestov and N. A. Osipova

The sulfonic acids of benzene and of diphenyl sulfone behave completely differently when reduced at a dropping mercury electrode [1]. While benzene sulfonic acids have no waves, besides the base wave, in the potential range investigated (from −0.1 to −2.7 v), diphenyl sulfone and its sulfonic acids give clear waves on the polarogram for the recuction of the SO_2 group with a characteristic half-wave potential for each compound. This factor made it possible to study the conditions of benzene sulfonation from the point of view of the formation of sulfonic acids of diphenyl sulfone.

This paper describes an investigation of the possibility of using a polarographic method for determining sulfonic acids of sulfones, formed in the sulfonation of toluene, chlorobenzene and naphthalene.

Pure preparations were used for the work. It was established that sulfonic acids of toluene and chlorobenzene, similarly to benzene sulfonic acids, do not form any reduction waves, besides the base waves, on polarograms. The corresponding sulfones, for example 4,4'-dimethyldiphenyl sulfone and 4,4'-dichlorodiphenyl sulfone, give waves of SO_2 group reduction with characteristic half-wave potentials which are displaced in relation to the half-wave reduction potential of diphenyl sulfone in accordance with the effect of the substituents (Cl and CH_3 group): 4,4'-dichlorodiphenyl sulfone is reduced more readily and 4,4'-dimethyldiphenyl sulfone less readily than diphenyl sulfone ($-\varphi^{1}/_{2}$ is 2.12 v for diphenyl sulfone, 1.94 v for 4,4'-dichlorodiphenyl sulfone and 2.28 v for 4,4'-dimethyldiphenyl sulfone). The sulfonic acids of these sulfones are reduced in a more positive region than the corresponding sulfones (Table 1).

The difference in behavior in polarography between chlorobenzene and toluene sulfonic acids and that of the corresponding sulfone sulfonic acids indicates the formation of sulfone sulfonic acids during the sulfonation of toluene and chlorobenzene.

The reduction of naphthalene sulfonic acids at a dropping mercury electrode gives a more complex and interesting picture. All the naphthalene sulfonic acids investigated (in contrast to benzene derivatives) and dinaphthyl sulfone give characteristic waves on the polarograms and the reduction potential depends both on the number of sulfonic acid groups introduced into the naphthalene nucleus and on their position in the nucleus. An increase in the number decreases the magnitude of the potential necessary for the reduction of the sulfonic acid. Sulfonic acids with sulfonic acid groups in the α-position are reduced in a somewhat more positive region of potential than β-sulfonic acids isomeric to them. In all cases the sulfone group, SO_2, is also reduced in a more positive region of potential than the sulfonic acid taken for the preparation of sulfone.

The established fact that naphthalene sulfonic acids are reduced at a dropping mercury electrode, on the one hand, complicates the determination of dinaphthyl sulfone sulfonic acids in the presence of naphthalene sulfonic acids and, on the other hand, opens the interesting possibility of determining separate naphthalene sulfonic acids in mixtures.

TABLE 1

Half-Wave Potentials of Sulfone and Sulfonic Acid Derivatives of Benzene, Toluene and Chlorobenzene

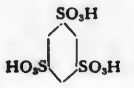
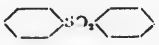
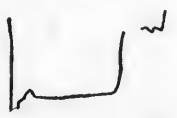
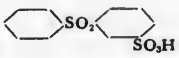
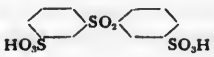
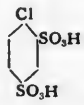
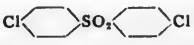
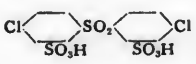
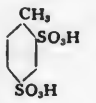
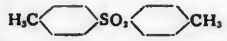
Exp. no.	Compound	Formula	Polarogram*	$-\varphi^{1}/_{2}$ (in v)
1	Benzene 1,3-disulfonic acid			—
2	Benzene 1,3,5-trisulfonic acid			—
3	Diphenyl sulfone			2.12
4	Diphenyl sulfone 3-sulfonic acid			1.90
5	Diphenyl sulfone 3,3'-disulfonic acid			1.82
6	Sulfonic mixture of benzene	—		1.82
7	Chlorobenzene 2,4-disulfonic acid			—
8	4,4'-Dichlorodiphenyl sulfone			1.94
9	4,4'-Dichlorodiphenyl sulfone X,X'-disulfonic acid			1.60
10	Sulfonic mixture of chlorobenzene	—		1.60

TABLE 1 (continued)

Expt. No.	Compound	Formula	Polarogram	$-\frac{1}{2}$ (in v)
11	4,4'-Dichloridiphenyl sulfone			—
12	4,4'-Dichlorodiphenyl sulfone X,X'-disulfonic acid			2.28
13	Sulfonic mixture of chlorobenzene	—		1.94

• In all the figures given in the article (polarograms), $\underline{i}$ (current strength) is plotted along the ordinate and φ (the imposed voltage with a minus sign) along the abscissa. The distance between two adjacent ordinates corresponds to 0.2 v.

•• This polarogram was plotted with a capillary with forced removal of the drop; the base was a 0.05 M aqueous solution of $N(C_2H_5)_4OH$ [anode potential equal to −0.1 v, compared with a saturated calomel electrode (s.c.e.)], while the polarogram of the sulfonic mixture of chlorobenzene was plotted with a normal capillary and the base used was a 0.05 M aqueous solution of $N(C_2H_5)_4I$ (anode potential equal to −0.27 v compared with an s.c.e). Therefore, on the polarograms given, the waves are displaced relative to each other, though they have the same $-\varphi_{1/2}$ compared with an s.c.e.

The possibility of applying a polarographic method for determining dinaphthylsulfone sulfonic acids in the presence of certain naphthalene sulfonic acids was proved on artificial mixtures of mono-, di- and trisulfonic acids of naphthalene with dinaphthyl sulfone disulfonic acid (Table 3). The polarogram clearly shows the reduction wave of dinaphthyl sulfone disulfonic acid with a characteristic potential $-\varphi_{1/2} = 1.64\text{-}1.67$ v. Naphthalene tetrasulfonic acid has a wave with a reduction potential very close to the reduction potential of dinaphthyl sulfone disulfonic acid, which has to be considered in polarographing sulfonic acids of the naphthalene series.

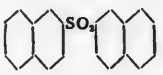
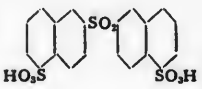
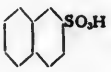
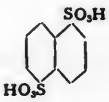
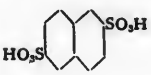
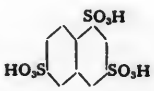
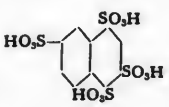
The application of polarography as an analytical method for investigating sulfonation reactions in the naphthalene series will require a more thorough study of the polarography of naphthalene sulfonic acids and a study of the behavior of individual components in mixtures of various compositions, which we propose to do in the near future.

EXPERIMENTAL

For the experiments we used pure products, which were identified by their melting points: the sulfones as they were and the sulfonic acids in the form of the corresponding sulfonyl chlorides. The sulfonyl chlorides were converted into the tetraethylammonium salts of the sulfonic acids by heating them for 2 hours with twice the theoretical amount of $N(C_2H_5)_4OH$ in aqueous solution. Base was added to the solutions of known concentration, obtained after hydrolysis, and the whole was diluted with water and used for plotting polarograms. The technical mixture of sulfonic acids, obtained after sulfonation of some compound (referred to later simply as the sulfonic mixture of the corresponding compound) was poured onto water and neutralized with $N(C_2H_5)_4OH$ to an alkaline reaction to brilliant yellow paper and after this base was added. In this way polarograms on the sulfonic mixtures in alkaline aqueous solutions were also plotted. Due to the insolubility of the sulfones in water, their

TABLE 2

Half-Wave Potentials of Sulfone and Sulfonic Acid Derivatives of Naphthalene

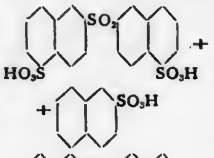
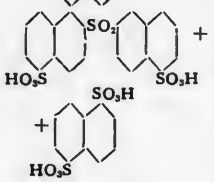
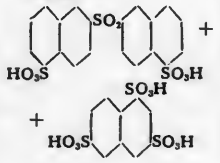
Exp. no.	Compound	Formula	Polarogram	$-\varphi_{1/2}$ (in v)
1	2,2'-Dinaphthyl sulfone			1.88
2	2,2'-Dinaphthyl sulfone 5,5'-disulfonic acid			1.64
3	Naphthalene 1-sulfonic acid			2.18
4	Naphthalene 2-sulfonic acid			2.26
5	Naphthalene 1,5-disulfonic acid			1.97 2.20
6	Naphthalene 2,6-disulfonic acid			2.18 2.46
7	Naphthalene 2,7-disulfonic acid			2.13
8	Naphthalene 1,3,6-trisulfonic acid			1.87 2.14
9	Naphthalene 1,3,5,7-tetrasulfonic acid			1.60 2.20 2.45

polarograms were plotted using solutions in 80% ethyl alcohol. As base, 0.05 M solutions of $N(C_2H_5)_4I$ or $N(C_2H_5)_4OH$ were used. The polarization curves were plotted with concentrations of the reducing substance of 0.001-0.002 M. The polarograms were plotted on an automatic Heyrovsky polarograph. We used a cell with an internal anode, whose potential was measured each time. The values of the potentials given are relative to a saturated calomel electrode.

As the sulfonic acids of naphthalene are reduced in the region of very negative potentials, we used a capillary with forced removal of the drop (a capillary with a paddle) to obtain cleaner polarograms of these compounds.

TABLE 3

Polarograms of Mixtures of 2,2'-Dinaphthyl Sulfone Disulfonic Acid* With Naphthalene Sulfonic Acids

Expt. no.	Compound	Formula	Polarogram	$-\varphi_{1/2}$ (in v)
1	Mixture of 2,2'-dinaphthyl sulfone 5,5'-disulfonic acid and naphthalene 2-sulfonic acid			1.64 2.19
2	Mixture of 2,2'-dinaphthyl sulfone 5,5'-disulfonic acid and naphthalene 1,5-disulfonic acid			1.67 1.97 2.15
3	Mixture of 2,2'-dinaphthyl sulfone 5,5'-disulfonic acid and naphthalene 1,3,5-trisulfonic acid			1.67 1.83

* We used 2,2'-dinaphthyl sulfone disulfonic acid, which was not isolated from the sulfonic mixture (see explanation to Table 2).

In Tables 1 and 2 the half-wave potentials and polarograms of the sulfones and sulfonic acids investigated are given.

4,4'-Dichlorodiphenyl sulfone disulfonic acid is not described in the literature. We prepared it by sulfonation of 4,4'-dichlorodiphenyl sulfone with high percent oleum, containing sufficient SO_3 to introduce two sulfonic acid groups (11 g of 64% oleum to 10 g of sulfone), at 120° over a period of 3 hours. The sodium salt of the sulfonic acid obtained was converted into the sulfonyl chloride by the usual method. This was recrystallized from toluene to a constant melting point, which did not change on further recrystallization. The sulfonyl chloride we obtained had m. p. 229.5-230° (with decomp.).

The dichlorodiphenyl sulfone disulfonic acid was also formed as a side product during the sulfonation of chlorobenzene to its disulfonic acid with high percent oleum at 120° for 3 hours (42.6 g of 62% oleum to 14.8 g of chlorobenzene). Its presence is obvious from the appropriate polarogram, on which a wave appears with $-\varphi_{1/2}$, corresponding to the $-\varphi_{1/2}$ of pure 4,4'-dichlorodiphenyl sulfone disulfonic acid.

In the polarographic examination of the sulfonic mixture of toluene, obtained by sulfonation of toluene with high percent oleum at 80° for 3 hours (53 g of 62% oleum to 15 g of toluene), a wave was discovered with $-\varphi_{1/2}$ = 1.94 v. The sulfonic acids of toluene do not give any waves on polarograms and sulfones as such were absent from the sulfonic mixture (on diluting the sulfonic mixture with water there was no precipitate formed); we could only assume that the wave mentioned was connected with sulfonated toluene sulfones, which was also corroborated by the value of the half-wave potential, which was displaced toward more positive potentials compared with $-\varphi_{1/2}$ of 4,4'-dimethyldiphenyl sulfone. As we established from the example of diphenyl sulfone, 4,4'-dichlorodiphenyl sulfone and their sulfonic acids, on introducing two sulfonic acid groups into a sulfone molecule, there is a shift in half-wave potential toward more positive values by approximately 0.3 v.

As was indicated in the general section, the sulfonic acids of naphthalene themselves give waves on polarograms for the reduction of the SO_3H groups. In Table 2 are given the values of $-\varphi_{1/2}$ for each of the naphthalene and dinaphthyl sulfone sulfonic acids examined and also the corresponding polarograms.

2,2'-Dinaphthyl sulfone 5,5'-disulfonic acid was not isolated in the pure form. Dinaphthyl sulfone was sulfonated under conditions which lead predominantly to the formation of the 5,5'-disulfonic acid [2] and polarograms were plotted on the sulfonic mixture obtained.

All the naphthalene disulfonic acids gave waves which differed from each other even in superficial appearance. On a polarogram the 1,5-disulfonic acid gave two waves which were quite sharply separated from each other. The 2,6-disulfonic acid gave a very strongly elongated wave, in which two waves could be distinguished with difficulty. Finally, the 2,7-disulfonic acid gave one wave.

Dinaphthyl sulfone disulfonic acid was clearly determined in the presence of mono-, di- and trisulfonic acids of naphthalene. We prepared artificial mixtures of these compounds, taken in equal concentrations, and plotted their polarograms. The experiments are summarized in Table 3.

SUMMARY

1. We determined the reduction potentials of 4,4'-dimethyldiphenyl sulfone, 4,4'-dichlorodiphenyl sulfone and 2,2'-dinaphthyl sulfone.

2. We established that toluene and chlorobenzene sulfonic acids were not reduced at a dropping mercury electrode in the potential region of −0.1 to −2.7 v, which makes it possible to determine the corresponding sulfones and their sulfonic acids in the sulfonation products of toluene and chlorobenzene.

3. It was established that naphthalene sulfonic acids of various degrees of sulfonation were reduced at a dropping mercury electrode and we determined the half-wave potentials of 7 naphthalene sulfonic acids.

The difference in the reduction potentials of individual naphthalene sulfonic acids makes it possible to use polarography for the study of naphthalene sulfonation reactions.

LITERATURE CITED

[1] E. S. Levin, A. P. Shestov, Proc. Acad. Sci. USSR, 96, 999 (1954); A. P. Shestov, J. Gen. Chem. 26, 1219 (1956)*; A. P. Shestov, N. A. Osipova, J. Gen. Chem. 26, 2866 (1956).*

[2] V. V. Kozlov, G. S. Tubyanskaya, Proc. Acad. Sci. USSR, 58, 233 (1947).

Received September 20, 1956

K. E. Voroshilov Research Institute on Organic Semiproducts and Dyes

*Original Russian pagination. See C. B. Translation.

PREPARATION OF DIFLUOROKETENE AND ITS POLYMER

N. N. Yarovenko, S. P. Motornyi and L. I. Kirenskaya

In recent years polymers of fluorinated olefins have aroused great interest due to their increasing value in various branches of industry. In connection with this, it seemed interesting to establish how much the properties of tetrafluoroethylene and its polymer change on substituting oxygen for two fluorine atoms.

$$CF_2{=}CF_2 \longrightarrow CF_2{=}C{=}O$$

Until recently, difluoroketene and all other dihalogen ketenes were unknown. The attempts by Staudinger and others to prepare dihalogen ketenes were unsuccessful [1].

The purpose of this work was to find a method for synthesizing difluoroketene and its polymer.

Difluoroketene could be synthesized by dehalogenation of difluorochloroacetyl bromide.

$$CF_2ClC(=O)Br \xrightarrow{Zn} CF_2{=}C{=}O$$

Difluorochloroacetyl bromide was dehalogenated in an ether medium with zinc dust, activated with copper. It is known that in preparing ketene not containing fluorine in ether solutions, it is practically impossible to separate it from the ether [2]. Difluoroketene also behaves analogously – it distils with the ether. As is known, acetamide is formed on passing dry ammonia into an ether solution of ketene and, analogously, difluoroacetamide was formed by reacting difluoroketene with ammonia.

$$CF_2C{=}O \xrightarrow{NH_3} CHF_2C(=O)NH_2$$

In the dehalogenation of difluorochloroacetyl bromide, besides the difluoroketene, difluoroketene polymer was also formed and did not distil with the ether.

The difluorochloroacetyl bromide required for this reaction was not described previously but it was readily prepared by reacting difluorochloroacetic acid salts with phosphorus tribromide.

Difluorochloroacetic acid may be prepared by chlorinating difluoroacetic acid [3], by reacting difluorodichloromethane with carbon monoxide [4], or by oxidizing halogenated propylenes [5]; however, we found a new simple method for preparing the esters of difluorochloroacetic acid, which consisted of reacting trichloroacetic esters with antimony trifluoride in the presence of antimony pentachloride.

$$CCl_3CO_2CH_3 \xrightarrow{SbF_3+SbCl_5} CF_2ClCO_2CH_3$$

For the reaction to succeed it is essential to mix the fluorinating reagents (SbF_3 + $SbCl_5$) thoroughly till the addition of the trichloroacetic esters, as is done during the fluorination of polychlorinated dialkylsulfides [6].

In the presence of bromine the reaction of trichloroacetic esters with antimony trifluoride stopped at the formation of the fluorodichloroacetic ester [7], although in the case of tribromoacetic esters, as we established, the reaction may proceed in the presence of bromine to the formation of the difluorobromoacetic ester.

EXPERIMENTAL

Preparation of difluorochloroacetyl bromide. 135 g of phosphorus tribromide was added to 100 g of barium difluorochloroacetate, cooled in ice water, and then the reaction mixture was heated for 3 hours at 160°. The difluorochloroacetyl bromide liberated during the course of the reaction was trapped in a receiver, protected from the moisture in the air. The distillate was then redistilled. The yield of difluorochloroacetyl bromide was 45 g (47.5%).

B. p. 49°, n_D^{20} 1.3864, d_4^{20} 1.8267.
Found %: C 13.19; Cl 18.12; Br 41.81; F 19.65. $C_2OClBrF_2$. Calculated %: C 12.4; Cl 18.3; Br 41.29; F 19.7.

Preparation of difluoroketene and its polymer. Into a 250 ml flask, fitted with a reflux condenser and a dropping funnel, was placed 60 g of zinc dust activated with copper and 100 ml of ether. Then a solution of 30 g of difluorochloroacetyl bromide in 20 ml of ether was slowly added, dropwise. Heat was evolved during the reaction. At the end of the reaction the ether solution was separated from the precipitate and distilled, at first at atmospheric pressure and towards the end, at a pressure of 13 mm. The difluoroketene monomer distilled with the ether at 34-36° and the difluoroketene polymer at 72° (102 mm). The yield of difluoroketene (in ether solution) was 10.5 g and the polymer 1.1 g, a total of 11.6 g (96%).

The difluoroketene polymer was a colorless, mobile liquid which in some cases turned into a viscous mass on standing.

B. p. 72° (105 mm), n_D^{24} 1.3610.
Found %: C 30.27; F 47.56. $(C_2OF_2)_n$. Calculated %: C 30.56; F 48.7.

In the ether solution of difluoroketene (b. p. 34-36°):

Found %: C 59.58; F 6.51. 14% solution of C_2OF_2. Calculated %: C 60.0; F 7.0.

The difluoroketene in ether solution was identified as difluoroacetamide.

29 g of the ether solution of difluoroketene was saturated with dry ammonia and then the ether distilled off at room temperature. The crystals of difluoroacetamide obtained were distilled under reduced pressure, when they had b. p. 105° (35 mm) and m. p. 52°.

A mixed melting point with difluoroacetamide prepared by the usual method was not depressed.

Preparation of methyl difluorochloroacetate. 150 g of antimony trifluoride was placed in a 1 liter Wurtz flask, carefully stirred with 10 ml of antimony pentachloride and 135 g of methyl trichloroacetate added. Then the reaction mixture was heated over a naked flame. The reaction products distilling off were trapped in a receiver, cooled to −20°. The mixture of fluorinated esters and starting material obtained was successively washed with dilute hydrochloric acid, a weak solution of sodium carbonate and water and distilled on a column after drying with calcium chloride. The yield of methyl difluorochloroacetate was 21 g (19%).

B. p. 79-81°, n_D^{18} 1.3460, d_4^{18} 1.3701, MR_D 22.7; calc. 22.3.
Found %: C 24.95; H 2.25; Cl 24.57; F 26.0. $C_3H_3O_2ClF_2$. Calculated %: C 24.90; H 2.07; Cl 24.6; F 26.3.

Preparation of methyl difluorobromoacetate. Into a 500 ml copper flask was placed 153 g of methyl tribromoacetate, 60 g of antimony trifluoride and 50 g of bromine. After the reagents were mixed thoroughly, the mixture was heated on a sand bath at 120° for 2 hours. Then the reaction products were distilled off and washed with water, the bromine neutralized with hyposulfite solution and the product dried with calcium chloride and distilled on a column. The yield of methyl difluorobromoacetate was 7.5 g (8.1%).

B. p. 96°, n_D^{28} 1.3880, d_4^{28} 1.7125, MR_D 25.41; calc. 25.27.
Found %: C 19.18; H 1.84, Br 42.42; F 19.61. $C_3H_3O_2BrF_2$. Calculated %: C 19.05; H 1.59; Br 42.33; F 20.10.

SUMMARY

1. The polymer of difluoroketene and an ether solution of the monomer were obtained by reacting difluorochloroacetyl bromide with zinc dust activated with copper. The monomer solution reacted with ammonia to give difluoroacetamide.

2. It was shown that reaction of trichloro- or tribromoacetic esters with antimony trifluoride in the presence of catalysts gave the esters of difluorochloro and difluorobromoacetic acid, respectively.

LITERATURE CITED

[1] H. Staudinger, E. Anthes, H. Schneider, Ber. 46, 3539 (1913).

[2] H. Staudinger, H. W. Kleve, Ber. 41, 594 (1908).

[3] F. Swarts, Zbl. 1906, I, 1231.

[4] U. S. Pat. 2378048.

[5] A. L. Henne, J. Alderson, M. S. Newman, J. Am. Chem. Soc. 67, 918 (1945).

[6] W. E. Truce, G. H. Birum, E. T. McBee, J. Am. Chem. Soc. 74, 3594 (1952).

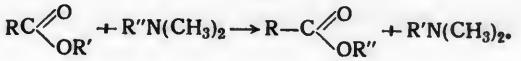
[7] Gryszkiewicz-Trochimowski, A. Sprozymski, J. Whnuk, Rec. trav. chim. 66, 419 (1947).

Received July 26, 1956

A STUDY OF THE MECHANISM OF THE REACTION OF TERTIARY AMINES WITH ESTERS*

S. V. Vitt and R. V. Kudryavtsev

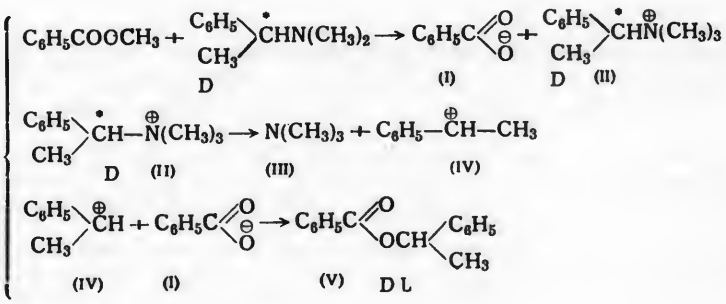
The purpose of this work was to study the mechanism of the reaction of tertiary amines with esters, which lead to an exchange of radicals between the ester and the amine [1-4]:



In order to solve the problem of the R" radical transference from nitrogen to oxygen, we studied the reaction of optically active D-N-dimethyl-α-phenethylamine with methyl benzoate.

If, as proposed by Eliel and Anderson in 1952 [3], the first stage of the reaction is ammonium salt formation, then further reaction of the acid anion (I) and the ammonium cation (II) may proceed in two directions. In the first case (Scheme 1a) the ammonium cation first decomposes to form amine (III) and a carbonium ion (IV), which combines with the acid anion (I) to give α-phenethyl benzoate (V).

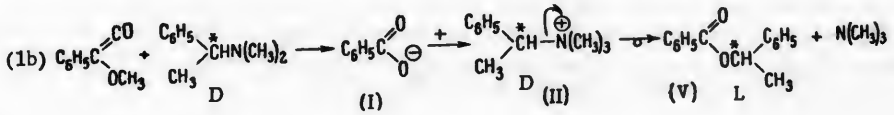
(1a)



If scheme (1a) is correct, then due to the planar structure of the carbonium ion (IV) the α-phenethyl benzoate formed must be racemic.

In the second case (scheme 1b) the α-phenethyl radical is transferred from the ammonium cation (II) to the acid anion (I) synchronously ("from hand to hand"); under these circumstances the configuration of the α-phenethyl radical must change to the opposite form.**

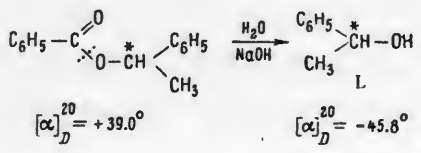
(1b)



*The authors are grateful to D. N. Kursanov, in whose laboratory the work was carried out, for his interest and valuable advice.

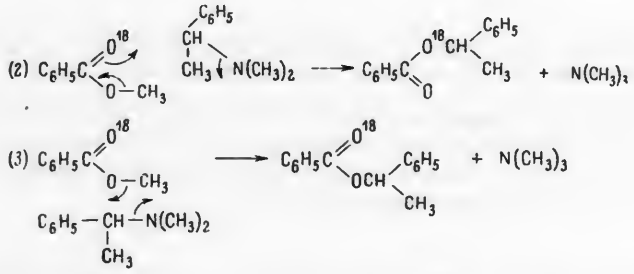
**The capacity of ammonium compounds containing an optically active radical to alkylate acid anions with a reversal of configuration was shown in 1949 by Snyder and Brewster [5].

In actual fact, it was found that during the process of this reaction the configuration of the α-phenethyl radical was reversed. This was proved by preparing the dextrorotatory α-phenethyl benzoate and its position in the L-series was established by the fact that its hydrolysis product was L-(−)-α-phenethyl alcohol [6].



This excluded the possibility of the given reaction proceeding through the intermediate stage of carbonium ion $C_6H_5-{}^{+}CH-CH_3$ formation.

However, scheme (1b) cannot be considered as the sole probable reaction scheme, as there are other possibilities of synchronous transfer of the α-phenethyl radical from nitrogen to oxygen inside an activated complex. This condition is fulfilled by the following schemes which describe the direct reaction of the ester with the amine, without preliminary formation of the ammonium salt.



In order to choose between the three reaction schemes examined (1b, 2 and 3), we used the heavy oxygen isotope, O^{18}. We carried out the reaction between N-dimethyl-α-phenethylamine and methyl benzoate containing an excess of the heavy isotope O^{18}, equal to 0.80 at. % in the carbonyl oxygen.

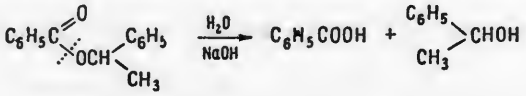
If scheme (1b) is correct, then the heavy oxygen isotope would be equally distributed in the two possible positions – carbonyl and ether – in the α-phenethyl benzoate formed as both oxygen atoms are equivalent in the acid anion and the probability of α-phenethyl radical addition is equal for both of them.

If the α-phenethyl radical is added to the carbonyl oxygen in a six-membered complex (scheme 2), then the α-phenethyl benzoate formed would contain all the excess heavy isotope in the ether position as the oxygen atoms in this case must exchange functions – the ether oxygen will become carbonyl and the carbonyl – ether.

If the α-phenethyl radical is added to the ether oxygen in a four-membered complex (scheme 3), then the α-phenethyl benzoate formed would contain the excess heavy oxygen isotope in the same position as the starting methyl benzoate, i.e., in the carbonyl.

An argument against this reaction scheme is the reversal of the phenethyl radical configuration noted by us, as, if the reaction actually proceeded through a four-membered complex, this would lead rather to a partial retention of the configuration.

After the reaction with labelled methyl benzoate, we obtained α-phenethyl benzoate and the total content of excess O^{18}, equal to 0.4 at. % had not changed. Then we had to determine the position of the excess heavy oxygen isotope. For this purpose, the α-phenethyl benzoate obtained was subjected to alkaline hydrolysis which, as the scheme shows, proceeded with breaking of the acyl oxygen bond.

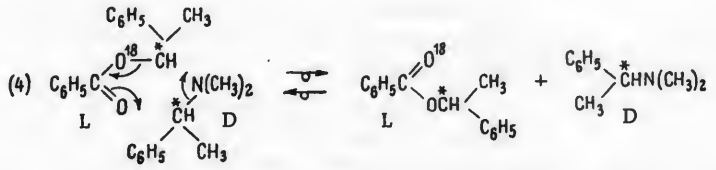


Isotopic oxygen analysis of the benzoic acid and α-phenethyl alcohol obtained by this method (see Table) indicated that after the reaction of the heavy oxygen isotope in α-phenethyl benzoate was distributed equally in both possible positions – in the ether and the carbonyl.

Substance	Percentage of excess O^{18}		
	total	in carbonyl	in the ether position
$C_6H_5C(=O^{18})-O-CH_3$ (starting)	0.38 0.42	0.8	0
$C_6H_5C(=O)-OCH(C_6H_5)CH_3$	0.39 0.41	0.4	0.4
$C_6H_5CH(CH_3)OH$ (after hydrolysis)	0.39 0.39 0.41	—	—
C_6H_5COOH (after hydrolysis)	0.19 0.19 0.20	—	—

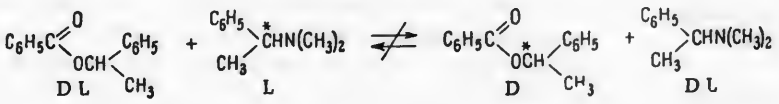
This fact eliminated the possibility of the reaction proceeding by scheme (2) and (3) and indicated that scheme (1b) was the most probable reaction scheme.

However, if this reaction proceeded by scheme (2) and the α-phenethyl benzoate being formed reacted with the still unreacted N-dimethyl-α-phenethylamine and if this secondary reaction also occurred in a six-membered transition complex,



then the repetition of this reaction would also result in the averaging of the oxygen-isotope content between the two possible positions and would also give an optically active α-phenethyl benzoate with a reversed configuration of the α-phenethyl radical.

In order to solve the possibility of a multiple reaction occurring by scheme (4), we reacted racemic α-phenethyl benzoate with optically active L-N-dimethyl-α-phenethylamine under the same conditions (195°, 18 hours). The configuration of the N-dimethyl-α-phenethylamine isolated after the reaction, was 96% retained, while at the same time the α-phenethyl benzoate remained racemic, which meant that the reversible reaction in effect did not occur.*



Thus, the reversal of the configuration of the α-phenethyl radical observed by us in the reaction of D-N-dimethyl-α-phenethylamine with methyl benzoate, which appears as an equalization of the function of the oxygen and proved by us isotopically, indicates completely unequivocally that this reaction is accompanied by the intermediate

* This is of some interest in itself as it indicates the limits of applicability of this reaction.

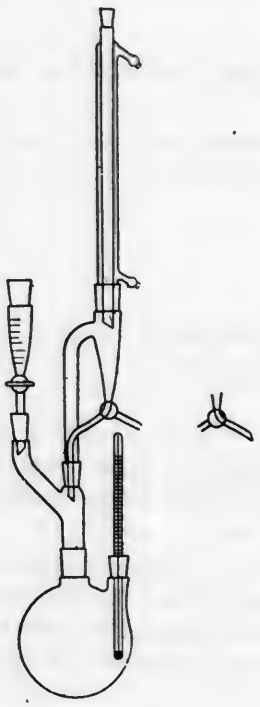
formation of the N-trimethyl-α-phenethylammonium cation and the benzoic acid anion. The transfer of the α-phenethyl radical from nitrogen to oxygen proceeds by scheme (1b).

EXPERIMENTAL

1. Malic acid. On treating the calcium salt of L-malic acid with sulfuric acid, Buck and Mottern [10] obtained a solution containing up to 67% of L-malic acid; however, they were unable to isolate crystalline L-malic acid.

We evaporated down in vacuum an aqueous solution obtained from 1 mole of pure acid calcium L-malate treated with dilute sulfuric acid until we obtained a thick syrup, which was then dissolved in 500 ml of pure acetone. The solution obtained was filtered to remove insoluble salts. The acetone was evaporated off in vacuum and the solid L-malic acid remaining dissolved in a mixture of 200 ml of acetone and 150 ml of ether (the ether may be replaced by benzene). An insignificant inorganic residue remained and was rejected. After distillation of the solvent (in vacuum) pure L-malic acid remained and this burnt without residue on a spatula. The yield was 90-93% and the m. p. 99-100°.

2. DL-Phenethylamine. The method usually used for the preparation of DL-phenethylamine [11], is unsuitable for the preparation of large amounts of this material.



Apparatus for the preparation of α-phenethylamine.

It proved to be convenient to prepare α-phenethylamine from acetophenone and commercial formamide in the presence of formic acid in the apparatus illustrated in the figure.

3 mole of acetophenone and 10.6 mole of formamide was heated at a temperature of up to 190° for 9 hours. During this time, 3 mole of 85 formic acid was added at a constant rate. The water formed during the reaction was collected in a water-trap and periodically removed through a two-way tap, while the acetophenone was returned to the reaction mixture.

After working up in the usual way and a distillation on a column 80 cm high, we obtained 294 g (81%) of α-phenethylamine with b. p. 81-82° (18 mm), n_D^{20} 1.5282.

3. The resolution of DL-phenethylamine was achieved by the method described in the literature [7] using L-malic acid. The D-α-phenethylamine used in the present work had a specific rotation of $[\alpha]_D^{25}$ + 39.5° (without solvent), which corresponds to 100% optical purity.

4. D-N-Dimethyl-α-phenethylamine we obtained by methylation of pure D-α-phenethylamine or its salt with L-malic acid, obtained directly from the resolution of DL-phenethylamine into antipodes [12]. The latter method was more convenient.

A mixture of 156 g of the pure salt of D-α-phenethylamine and L-malic acid, 180 ml of 85% formic acid and 175 ml of 30% formalin was heated on a boiling water bath for 10 hours, after which the mixture was cooled and 75 ml of concentrated hydrochloric acid added; the formic acid and water were distilled off in vacuum. The residue was dissolved in water, made alkaline with 4 N sodium hydroxide and steam-distilled. The distillate (about 700 ml) was treated (with shaking) with 20 ml of acetic anhydride, then made alkaline and the amine liberated extracted with benzene. The benzene solution was dried with solid potassium hydroxide. Distillation on a column gave 73.2 g (81%) of D-N-dimethyl-α-phenethylamine:

B. p. 78-78.5° (15 mm), $n_D^{19.5}$ 1.5024, d_4^{20} 0.9027, $[\alpha]_D^{23}$ from 70.8 to 71.6° (without solvent); methiodide, m. p. 157-157.5°; $[\alpha]_D^{20}$ + 12.3° (in water, c = 8.8).

5. Preparation of methyl benzoate, containing excess O^{18} in the carbonyl group was carried out by the scheme:

$$C_6H_5C{\equiv}N + CH_3OH + HCl \rightarrow C_6H_5{-}C(=\overset{\oplus}{N}H_2Cl^{\ominus}){-}OCH_3 \xrightarrow{H_2O^{18}}$$
$$\rightarrow C_6H_5{-}C(=O^{18}){-}OCH_3 + NH_4Cl.$$

18.0 g of dry hydrogen chloride was introduced into a mixture of 45.5 g of benzonitrile and 20.5 g of anhydrous methyl alcohol, cooled in ice. After standing for 2 days in a refrigerator, the imido-ester hydrochloride was ground with absolute ether, quickly sucked off and transferred to a flask into which had previously been placed 50 ml of absolute ether and 15 ml of H_2O^{18} (excess concentration of O^{18} 0.80 at. %). After standing for 7 days, the ether solutions was decanted from the solid salts, washed with water and dried with potassium carbonate.

We obtained 51.0 g (85%, calculated on the benzonitrile) of methyl benzoate $-O^{18}$:

B.p. 52° (3 mm), n_D^{20} 1.5170, d_4^{20} 1.0882 [8].

6. DL-α-phenethyl benzoate was prepared by the scheme:

$$C_6H_5{-}CHO \xrightarrow[H_2O]{CH_3MgI} C_6H_5{-}CH(OH){-}CH_3 \xrightarrow[C_5H_5N]{C_6H_5COCl} C_6H_5{-}CH(O{-}C(=O){-}C_6H_5){-}CH_3$$

and had the constants:

B. p. 174-179° (12 mm), n_D^{20} 1.5617, d_4^{20} 1.0968.

7. The reaction of methyl benzoate $-O^{18}$ with D-N-dimethyl-α-phenethylamine goes by the reaction

$$C_6H_5C(=O^{18})OCH_3 + \underset{CH_3}{\overset{C_6H_5}{}}\!\!>\!CHN(CH_3)_2 \rightarrow C_6H_5C(=O)OCH\!<\!\underset{CH_3}{\overset{C_6H_5}{}} + N(CH_3)_3$$

D L

A mixture of 6.8 g of methyl benzoate $-O^{18}$ and 8.15 g of D-N-dimethyl-α-phenethylamine was heated at 195 ± 3° for 18 hours in an atmosphere of nitrogen. The reaction mixture was dissolved in 20 ml of benzene, the benzene solution washed with 50 ml of 1 N sulfuric acid, water and soda solution and dried with anhydrous magnesium sulfate.

After 2 distillations using a pear fractionating column, 8 cm high, the benzene solution yielded 5.21 g of α-phenethyl benzoate:

B. p. 155-156° (5 mm), n_D^{20} 1.5581, d_4^{20} 1.091 , $[\alpha]_D^{16}$ + 39.0 ± 0.5 (in acetone c = 18.6).

3.72 g of the (+)-α-phenethyl benzoate obtained was hydrolyzed by boiling with 15 ml of 4 N sodium hydroxide for 4 hours. The reaction mixture was extracted with methylene chloride (3 × 15 ml) and the extract obtained dried with anhydrous magnesium sulfate. After 2 distillations, we obtained 1.27 g of L-(−)-α-phenethyl alcohol:

B. p. 97-98° (17 mm), n_D^{20} 1.5270, $[\alpha]_D^{25}$ −45.8 ± 0.5° (in dioxane, c = 5.85).

After extraction with methylene chloride, the aqueous layer was acidified with a slight excess of dilute sulfuric acid, the benzoic acid extracted with benzene, the excess benzene distilled off and hexane added. After filtering and drying, the precipitate had m. p. 121-122°.

The results of isotopic analysis of the α-phenethyl alcohol and the benzoic acid are given in the table.

All the isotopic analyses were carried out by the method developed by I. P. Gragerov [9]. The substance was cracked in vacuum at a temperature of 700-800°. The carbon dioxide thus formed was distilled off and analyzed mass-spectrometrically.

8. Examination of the possibility of a reaction between DL-α-phenethyl benzoate and L-N-dimethyl-α-phenethylamine. 6.3 g of DL-α-phenethyl benzoate [b. p. 174-179° (12 mm), n_D^{20} 1.5617, d_4^{20} 1.0968] and 4.2 g of L-(−)-N-dimethyl-α-phenethylamine [b. p. 87-87.5° (23 mm), n_D^{20} 1.5040, d_4^{20} 0.9042, $[\alpha]_D^{25}$ + 40.8°] were heated for 18 hours at 195 ± 2°. The reaction mixture was treated with excess 15% sulfuric acid and the aqueous solution washed several times with benzene and then made strongly alkaline to phenolphthalein. The amine liberated was extracted with benzene, the benzene solution dried with solid potassium hydroxide and the amine distilled after distilling off the benzene. We isolated 3.0 g of amine:

B. p. 80° (15 mm), n_D^{20} 1.5030, d_4^{20} 0.9038, $[\alpha]_D^{25}$ −39.3°.

The configuration of the amine was 96% retained during this procedure.

The benzene solution, remaining after the extraction of the amine, was washed with bicarbonate solution and then water. After drying and distilling off the benzene, the DL-α-phenethyl benzoate was distilled:

B. p. 143-145° (4 mm), n_D^{20} 1.5608, $[\alpha]_D^{25}$ 0 ± 0.3°.

SUMMARY

1. We studied the mechanism of the reaction of tertiary amines with esters using as an example the reaction of methyl benzoate, labelled in the carbonyl with a heavy oxygen isotope, and optically active D-(+)-N-dimethyl-α-phenethylamine.

2. It was shown that the first stage of the reaction is ion formation – benzoic acid anion and N-trimethyl-α-phenethylammonium cation.

3. It was shown that transfer of the α-phenethyl radical from nitrogen to oxygen occurs with a reversal of configuration.

4. We studied the possibility of a secondary reversible reaction between α-phenethyl benzoate and N-dimethyl-α-phenethylamine. It was shown that this reaction practically did not occur under the given conditions of the reaction of methyl benzoate and N-dimethyl-α-phenethylamine.

5. The synthesis of methyl benzoate, labelled in the carbonyl with a heavy oxygen isotope, is described.

6. The preparation of crystalline malic acid from its acid calcium salt is described.

7. The preparation of DL-α-phenethylamine and its conversion into D- and L-N-dimethyl-α-phenethylamine is described.

LITERATURE CITED

[1] H. R. Snyder, E. L. Eliel, J. Am. Chem. Soc. 71, 663 (1949).

[2] H. R. Snyder, E. L. Eliel, R. E. Carnahan, J. Am. Chem. Soc. 72, 2958 (1950).

[3] E. L. Eliel, R. P. Anderson, J. Am. Chem. Soc. 74, 547 (1952).

[4] E. L. Eliel, T. N. Ferdmann, J. Org. Ch. 19, 1693 (1954).

[5] H. R. Snyder, J. H. Brewster, J. Am. Chem. Soc. 71, 291 (1949).

[6] E. D. Hughes, C. K. Ingold, A. D. Scott, J. Chem. Soc. 1937, 1201.

[7] Synth. Org. Prep. 2, 526 (1949).

[8] M. L. Bender, J. Am. Chem. Soc. 73, 1626 (1951).

[9] I. P. Gragerov, Report to the All-Soviet Conference on the Use of Isotopes in Catalysis. Moscow, March-April, 1956.•

[10] R. E. Buck, H. H. Mottern, Ind. Eng. Chem. 39, 1087 (1947).

[11] Synth. Org. Prep. 2, 523 (1949); B. M. Bogoslovsky, Reactions and Methods of Investigation of Organic Compounds, 3, 253 (1954).•

[12] D. N. Kursanov and S. V. Vitt, Proc. Acad. Sci. USSR, 113, 607 (1957).••

Received June 28, 1956

• In Russian.

•• Original Russian pagination. See C. B. Translation.

REACTION OF THE SIMPLEST OLEFINS WITH AQUEOUS SOLUTIONS OF FORMALDEHYDE AND ACETALDEHYDE*

M. I. Farberov, Ya. I. Rotshmein, A. M. Kutin and N. K. Shemyakina

A large number of patents [1] are devoted to the reaction of the simplest olefins of the aliphatic series with aldehydes. However, in spite of the wide possibilities for industrial synthesis on this basis, the problem is little dealt with in the scientific literature.

Prins [2] was the first to investigate the reaction between formaldehyde (in the form of paraformaldehyde) and some olefins of the aromatic and terpene series (styrene, anethole, pinene, camphene) in the presence of sulfuric acid as catalyst and using glacial acetic acid as solvent. This work was more of an exploratory character and the reaction products were not identified quite accurately (which Fourneau et al. also reported [3]).

Working under the same conditions as Prins, Baker [4] passed propylene at 35° into a solution of paraformaldehyde in glacial acetic acid in the presence of 10% sulfuric acid. With this, he obtained butanediol-1,3 diacetate as the main product and 4-acetoxytetrahydropyran and 4-methyldioxane-1,3 in smaller amounts. Arundale and Mikeska [1] carefully collected in a long review article all the material (mainly patents) devoted to condensations of olefins with aldehydes and the use of the reaction products in organic synthesis. They also gave in a summarized version the results of their unpublished work on the reaction of isobutylene and propylene with formaldehyde and isobutylene with acetaldehyde.

This work is devoted to the study of the reaction of the simplest olefins (propylene and butylene) with the simplest aldehydes. The reaction was carried out with aqueous solutions of aldehydes in the presence of dilute sulfuric acid (in most experiments the concentration of sulfuric acid was 1.5-5%). The reaction temperature was varied with the amount of olefin taken within the range of 80-125°; the pressure was 8-14 atm for butylene and 35-50 atm for propylene.

Under these conditions the main reaction products were alkyldioxanes-1,3 in 78-85% yields. Besides this, cyclic alcohols and diols and traces of unsaturated alcohols were detected in the reaction products.**

In reacting propylene with formaldehyde (Scheme 1) the main reaction product (80-85%) was 4-methyldioxane-1,3 (I) besides a certain amount (7-8%) of 4-hydroxytetrahydropyran (II) and butanediol-1,3 (3-5%) (III). Besides this, traces of allylcarbinol (IV) (0.4-0.6%) were also detected in the reaction products.

The structure of (I) was confirmed by its conversion into (III) when hydrolyzed in the presence of excess methyl alcohol (methanolysis) and a small amount of sulfuric acid. The methyl alcohol bound the formaldehyde formed in the form of methylal and displaced the equilibrium toward the formation of (III) [5].

(II) was identical to the product obtained by reacting allylcarbinol with formaldehyde in an acid medium [6]. The structure of (II) was also confirmed by oxidation of tetrahydro-γ-pyrone (V) and by a series of other reactions.

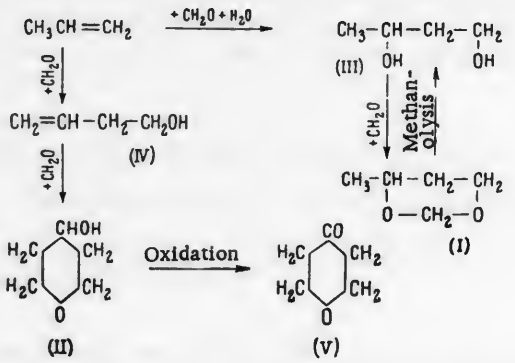
(III) and (IV) were identified by the known constants of these compounds.

A thorough study of the reaction of the simplest olefins with aldehydes using a series of examples showed that two series of products were formed. For example, in reacting propylene with formaldehyde the main primary

*The work was carried out in the period 1945-1948.

**Further on the yields are indicated for optimal working conditions, calculated on the reacted aldehyde.

Scheme 1



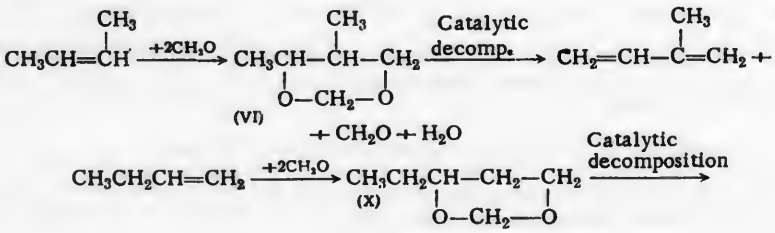
reaction product was butanediol-1,3 (III), which then reacted with formaldehyde to give 4-methyldioxane-1,3 (I), which is the formal of the diol (III). As is known, acetal formation is an equilibrium reaction and the state of the equilibrium, with all other conditions equal, depends on the nature of the alcohol (diol) and the aldehyde [7]. This equilibrium is strongly displaced toward alkyldioxane formation.

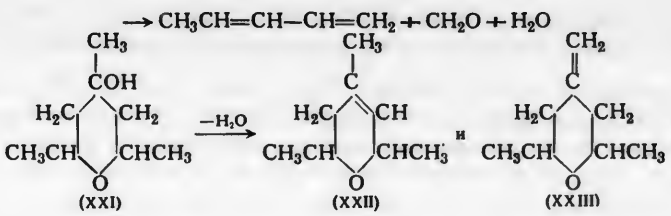
Another product formed in parallel with (III) was the unsaturated alcohol – allylcarbinol (IV), which was irreversibly converted into (II) by reacting further with formaldehyde; therefore, the amount of free unsaturated alcohol in the reaction products was very small. We were convinced that the reactions of (III) and (IV) formation were parallel [i.e., that (IV) was not a product of partial dehydration of (III)] by studying the conversion of (III) itself under the conditions of the main reaction; (III), taken separately did not undergo any noticeable conversions.

Butene-2 reacted analogously with formaldehyde. The main reaction product (90-92%) was 4,5-dimethyldioxane-1,3 (VI) with a certain amount (7-9%) of 3-methyl-4-hydroxytetrahydropyran (VII). An unsaturated alcohol was also detected in the reaction products. The structure of (VI) was confirmed by its smooth methanolysis into 2-methylbutanediol-1,3 (VIII). The structure of (VII) was proved by oxidizing it to 3-methyl-tetrahydro-γ-pyrone (IX).

In reacting a fraction of normal butylenes containing about 70% of butene-2 and 30% of butene-1 with formaldehyde, butene-2 formed (VI) as its main product while butene-1, apparently, gave 4-ethyldioxane-1,3 (X). Substances (VI) and (X) have practically the same constants; the difference in structure of these similar compounds was established beyond doubt by identifying the dienes obtained by their catalytic joint conversion. It is known that when passed over certain solid catalysts alkyldioxanes decompose to form dienes [1]. A mixture of (VI) and (X) was passed over a catalyst of this type in the presence of water vapor at 400-425°. A mixture of isoprene and piperylene was obtained in a yield of 65 mole % in a ratio approximately analogous to the amount of butene-2 and butene-1 in the starting mixture of olefins (Scheme 2).

Scheme 2

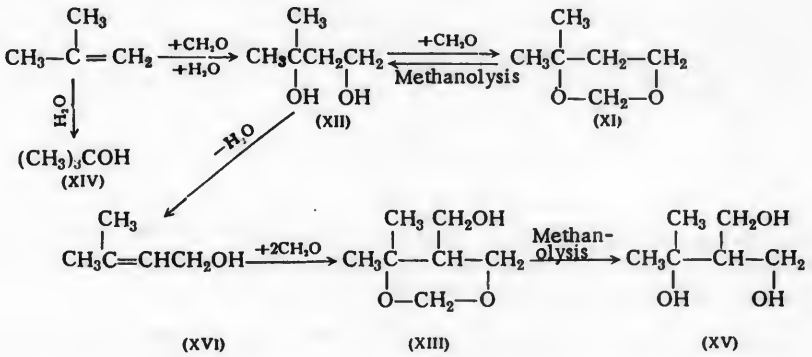




Isobutylene and formaldehyde react under the mildest conditions (temperature 85-90°; concentration of H_2SO_4 1-1.5%). The main reaction product (73-80% in this case, see Scheme 3) was 4,4-dimethyldioxane-1,3 (XI) besides a certain amount (7-10%) of 3-methylbutanediol-1,3 (XII) and the cyclic "dioxane" alcohol, 4,4-dimethyl-5-hydroxymethyldioxane-1,3 (7-8%)(XIII). An unsaturated alcohol was detected in the reaction products, but no derivative of hydroxytetrahydropyran. Under the reaction conditions a considerable amount of isobutylene (23-25% calculated on the reacted isobutylene) was hydrated to trimethylcarbinol (XIV).

The structure of (XI) was confirmed by its methanolysis to the diol (XII); this methanolysis did not proceed smoothly, however, and the yield of (XII) was not greater than 50% due to side-reactions [5]. Compound (XIII) has a hydroxyl group and dioxane ring. The hydroxyl group was determined by conversion into an acetate and the presence of the dioxane ring was confirmed by methanolysis with the liberation of methylal; under these conditions (XIII) was converted into a triol-2-hydroxymethyl-3-methylbutanediol-1,3 (XV) (Scheme 3).

Scheme 3



A study of the reaction of isobutylene with formaldehyde convinced us that, here, products of only one series are formed due, presumably, to the considerably greater rate of the main reaction, i.e., only methylbutanediol (XII) and products of its further conversions were obtained. Under the reaction conditions, (XII) underwent partial dehydration and was converted into 2-methylbuten-2-ol-4 (XVI). The latter reacted with formaldehyde to give a "dioxane" alcohol (XIII).

Other similar olefins reacted with formaldehyde as smoothly and under the same mild conditions as isobutylene, to give high yields of alkyldioxanes (up to 90%) as the main reaction products. 2-Methylbutene-2 gave, for example, 4,4,5-trimethyldioxane-1,3 (XVII), while α-methylstyrene gave 4-phenyl-4-methyldioxane-1,3 (XVIII).

Of the olefins only isobutylene (and certain other similar olefins) reacted smoothly with acetaldehyde as in this case the reaction proceeded under mild conditions under which no side-reactions of the acetaldehyde took place. In this case, as well, we observed the phenomenon of dual reactivity; the main reaction product (90-92%) was the alkyldioxane, 2,4,4,6-tetramethyldioxane-1,3 (XIX), but besides it a certain amount (2-5%) of a hydroxytetrahydropyran derivative [2,4,6-trimethylhydroxytetrahydropyran (XXI)] was detected.

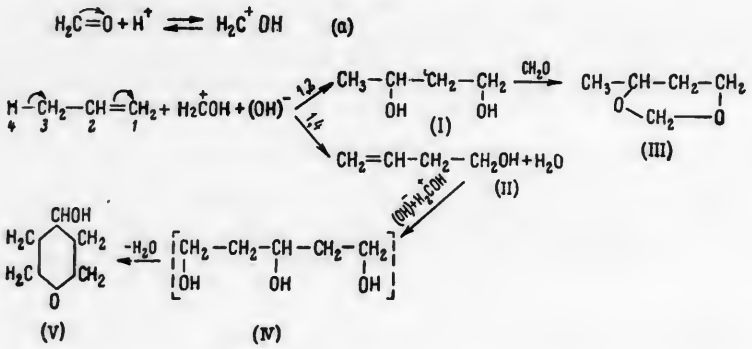
The structure of (XIX) was proved by methanolysis of 4-methylpentandiol-2,4 (XX); in this case as well the methanolysis did not proceed smoothly (with an 18-25% yield) due to side-reactions [5]. Dehydration of

(XXI) over anhydrous copper sulfate gave a mixture of (XXII) and (XXIII) (Scheme 2). Ballard et al. [8] obtained the substances (XXII) and (XXIII) in very small amounts by dehydrating (XX) and identified them.

The reaction of propylene and butene-2 with acetaldehyde required more drastic reaction conditions, which caused a series of side-reactions of acetaldehyde: resinification, formation of crotonaldehyde, the subsequent conversions of the latter, etc. The alkyldioxane yields were thus very small. The reaction proceeded somewhat better in the presence of zinc chloride in a solution of dichloroethane, but in this case as well, the alkyldioxane yield was only 10% for propylene and 50% for butene-2. Thus, 2,4,6-trimethyldioxane-1,3 was prepared from propylene and acetaldehyde, and 2,4,5,6-tetramethyldioxane-1,3 (XXIV) from butene-2 and acetaldehyde.

The reaction mechanism. The mechanism of the reaction of olefins with aldehydes as well as the phenomenon of dual reactivity discovered there may be explained on the basis of the ideas put forward by A. N. Nesmeyanov and M. I. Kabachnik [9]. The olefins examined are characterized by the presence of σ,π-conjugation which gives them a capacity for dual reaction at the 1,2 and 1,4 bonds. As an example, let us examine the reaction mechanism in the case of propylene reacting with formaldehyde (Scheme 4).

Scheme 4



According to the theory widely accepted at the present time on the mechanism of acid catalysis, the role of the acid is reduced to the formation of an intermediate carbonium ion. In this case, the acid produces the proton for the formation of a carbonium ion from formaldehyde (a).

The reaction proceeds mainly at the 1,2 bonds: the carbonium ion (a) is added to carbon atom 1; a positive carbonium reaction center forms on the 2nd carbon atom and by reacting with water it adds a hydroxyl ion (freeing a proton). Butanediol-1,3 (I) is formed as a result of 1,2 additions. Besides the main reaction, a parallel reaction also occurs. In this case, the addition of the carbonium ion (a) to carbon atom 1 is accompanied by the transfer of the reaction center to the 4th atom, the hydrogen atom 4 under these conditions is protonized and splits off to give water. This causes a break of not only the 1,2, but also the 3,4 bonds and the formation of a new bond between the 2 and 3 atoms. This mode of reaction leads to the formation of the allylcarbinol (II). The possibility of (II) formation by reacting propylene with formaldehyde is indicated in the literature [4].

The butanediol (I) and allylcarbinol (II) formed react further with formaldehyde in an acidic medium; under these conditions (I) is converted into methyl dioxane (III) and (II) forms of pentanetriol (IV) which readily loses water to close the six-membered ring, forming hydroxytetrahydropyran (V) [6]. The reactions occur analogously in the other cases, as well.

In reacting isobutylene with formaldehyde, in effect only 1,2 addition occurs (apparently due to the great rate of this reaction in this case). Only 3-methylbutanediol (XII) and products of its further reaction are obtained (Scheme 3).

EXPERIMENTAL

Apparatus. We studied the condensation of olefins with formaldehyde in an autoclave or on a batch operation column. The 1.5 liter autoclave made from BAZhM alloy was placed in a heating mantle fixed on

a shaking apparatus. The column was made of steel, 2400 mm high, with a copper tube of 40 mm internal diameter; between the lower flanges of the column was fitted a bronze bush with a Schott filter for bubbling in the olefin; the column was fitted with a jacket for heating and cooling.

Starting materials. The propylene fraction had an 85-88% propylene content. The isobutylene was prepared by dehydrating isobutyl alcohol and was then fractionated on a semi-industrial column. The isobutylene content was 98-99%.

The mixture of normal butylenes was prepared with semi-industrial apparatus after working up the "pseudo-butylene" fraction from the SK-1 plant with a solution of cuprammonium salts (to separate divinyl) and it contained 1.5% divinyl, 1% isobutylene, 30% butene-1 and 67.5% butene-2.

Butene-2 was prepared by carefully separating the mixture of normal butylenes to remove butene-1 on a semi-industrial column of 100 plates. Analysis (by infrared spectroscopy) showed traces of butene-1 in the butene-2 fraction obtained.

2-Methylbutene-2 was prepared by dehydrating tertiary amyl alcohol and had the constants: b. p. 38.4°, n_D^{15} 1.3908.

Formaldehyde was prepared by dissolving paraformaldehyde in water(35-40% solution). In some cases technical formalin containing 35-40 g of formaldehyde and 5-10 g of methanol per 100 liters was used.

The acetaldehyde used in the reaction with isobutylene was in the form of a 26% aqueous solution.

Treatment of the reaction products. The reaction mixture consisted of a two-layer liquid. The layers were separated, the amount of aldehyde in them was determined (by the hydroxylamine method) and the amount converted during the experiment was calculated. In the cases where the reaction was carried out with technical formalin containing methanol, the amount of formaldehyde used in converting the methanol into methylal was considered in calculating the conversion.

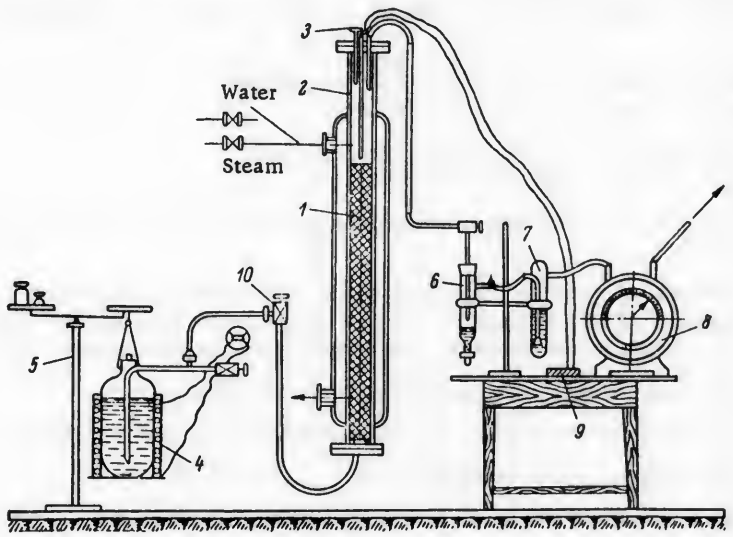


Diagram of the laboratory batch apparatus for condensing formaldehyde with olefins.
1) Packed batch operation column; 2) thermocouple socket; 3) inlet for loading; 4) tank with propylene; 5) scales; 6) drop separator; 7) alkali bubbler; 8) gas meter; 9) galvanometer; 10) control valve.

The lower, aqueous acid layer was extracted three times with chloroform (or dichloroethane). The extract was mixed with the upper, oily layer. The mixture obtained was treated with aqueous ammonia to bind the free formaldehyde and distilled on a column of 15 theoretical plates. After distilling off the chloroform,

we collected fractions of the reaction products. After several fractionations, very pure products were obtained. In addition, the alkyldioxane content was checked analytically by hydrolysis in the presence of hydroxylamine salts [5, 10].

The yields of the separate reaction products were calculated on the formaldehyde reacted.

The methanolysis of the alkyldioxanes was carried out with excess methyl alcohol in the presence of sulfuric acid (2.5-5% of the total mixture). The reaction was performed in a flask connected to the laboratory fractionating column. The methylal (acetal) was collected at 41-44° (57-60° for acetal). When the reaction ceased, the mixture was neutralized with sodium acetate or carbonate. The reaction products were then distilled.

The reaction conditions for various olefins with aldehydes and the reaction-product yields are given in Table 1. The constants and analyses of the compounds obtained are given in Table 2.*

Alkyldioxanes formed azeotropes with water; the boiling point of the azeotrope of (I) was 88°. The composition of the azeotrope was 76.75% (I) and 23.25% water. The solubility of (I) in water at 20° was 33.01 weight %; the solubility of water in (I) at 20° was 5.76%. The boiling point of the azeotrope of (XI) was 92.8°. The azeotrope composition was 65% (XI) and 35% water. The solubility of (XI) in water at 20° was 18%; the solubility of water in (XI) at 20° was 2.81%. The boiling point of the azeotrope of (XIX) was 92.5°. The azeotrope composition was 65.6% (XIX) and 34.4% water. The solubility of (XIX) in water at 20° was 3.38%.

The alkyldioxanes were identified by methanolysis to the corresponding diols [5]. The hydrolysis usually proceeded smoothly (with a yield of up to 88%); the dioxane derivatives in which the oxygen atom is bound to a tertiary carbon atom, i.e., (XI), (XIII) and (XX), hydrolyzed much less smoothly (18-38% yields).

The derivatives of hydroxytetrahydropyran (II) and (VII) were identified by oxidation to the corresponding ketones, the tetrahydro-γ-pyrones (V) and (IX). As an example we give the data on the oxidation of (VII) to (IX).

11.6 g of (VII) was added to a mixture of 30 ml of water and 13.5 g of 98% H_2SO_4 and then a solution of 8.5 of CrO_3 in 10 ml of H_2SO_4 was gradually added with cooling. The temperature was 25-29°. The reaction products were extracted with ether. The ether extract was dried and distilled several times (see Table 2 for the constants and analyses).

2,4-Dinitrophenylhydrazone for (V) m. p. 186.5-187° (from alcohol).
Found %: N 19.75. $C_{11}H_{12}O_5N_4$. Calculated %: N 20.00.

2,4-Dinitrophenylhydrazone for (VII) m. p. 193.5° (from alcohol).
Found %: N 19.3. $C_{12}H_{14}O_5N_4$. Calculated %: N 19.1.

For identification 2,4,6-trimethylhydroxytetrahydropyran (XXI) (with a hydroxyl group at the tertiary carbon atom) was dehydrated.

3 g of (XXI) was heated with 0.09 g of anhydrous $CuSO_4$ in a flask connected to a microcolumn. After drying the distillate, we obtained 1.5 g of a fraction which was a mixture of the pyran derivatives (XXII) and (XXIII) (see Table 2 for the constants and analysis). The bromine number was 123 (found) and 126.6 (calculated).

In order to identify some of the alcohols, we prepared their derivatives.

Allylcarbinol (IV) was characterized as the 3,5-dinitrobenzoate with m. p. 152° (from alcohol).

Found %: N 10.2. $C_{11}H_{10}O_6N_2$. Calculated %: N 10.5.

The acetate of (IV): b. p. 124.7-125.2°, d_4^{20} 0.9302, n_D^{20} 1.4206.

2-Methylbuten-2-ol-4 (XVI) was identified as the phenylurethan with m. p. 63-63.5° (from alcohol) (literature data: 63-64° [15]).

Found %: N 6.65. $C_{12}H_{15}O_2N$. Calculated %: N 6.83.

From the dioxane alcohol (XIII) we prepared the acetate: b. p. 128-129° at 15 mm, d_4^{20} 1.0920, n_D^{20} 1.4493, MR_D 46.20; calc. 46.50.

* K. A. Machtina carried out the experimental part of the reaction of isobutylene with acetaldehyde.

TABLE 1

The Reaction Conditions and Product Yields in the Reaction of Olefins With Aldehydes

	Reaction with formaldehyde			Isobutylene and acetaldehyde
	propylene	butene-2	isobutylene	
Apparatus	Column	Autoclave	Column	Autoclave
Experimental conditions				
Concentration of H_2SO_4 (g/100 ml) (in the aqueous aldehyde solution)	5	3	1.5	2
Temperature	108°	130°	85°	75°
Pressure (in atm.)	.36		7	
Reaction time (in min.)	240	105	180	180
Rate of olefin flow (in g/cm²) of the column's cross section	0.53	—	0.51	—
Taken for reaction (in g):				
olefin	1133	300	1715	82.3
aldehyde	599.9	188	750.8	109.2
Reacted (in g and in %):				
olefin	382		966 (see note 1)	(see note 1)
aldehyde	539.3 (85%)	177 (94%)	721.6 (96.1%)	74.3 (68.6%)
Yield (in g and in %) on aldehyde reacted:				
alkyldioxane	(I) 735.4 (80.4%)	(VI) 308 (90%)	(XI) 1022 (73.35%)	(XIX) 105.9 (90.4%)
cyclic alcohol (see note 2)	(II) 65.66 (7.16%)	(VII) 22.8 (6.0%)	(XIII) 92.6 (7.92%)	(XXI) 4 (22%)
diol	(III) (3.2%)	Not found	(XII) 176.20 (7.19%)	Not found
unsaturated alcohol	(IV) 8.52 (0.65%)	(1.3%)	(XVI) 14.30 (0.95%)	(1.5—2%)

1. A considerable amount of trimethyl carbinol (up to 23% on the isobutylene reacted) was obtained in the reaction of isobutylene with aldehydes; the former was isolated in the form of an azeotrope with water with b. p. 80°, d_4^{20} 0.8135 and n_D^{20} 1.3873.
2. Refers both to derivatives of hydroxytetrahydropyran (II), (VII) and (XXI) and to "dioxane" alcohol (XIII).

TABLE 2

Constants and Analyses of Compounds Obtained

Substance number	Name of compound and yield (in %)	Boiling point and pressure (in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Found (%) C	Found (%) H	Found (%) OH	Calculated (%) C	Calculated (%) H	Calculated (%) OH	Literature data
	Propylene and formaldehyde												
(I)	4-Methyldioxane-1,3 (80.4%)	115.3°	0.9758	1.4159	26.23	26.27	58.71	9.37		58.80	9.33		[6]
(II)	4-Hydroxytetrahydropyran (7.16%)	190	1.0708	1.4600	26.09	26.26							[11]
(III)	Butanediol-1,3 (3.2%)	203—204	1.0197	1.4433	23.41	23.72							[12]
(IV)	Allylcarbinol (0.65%)	114.5—115	0.8453	1.4212	21.63	21.73							
(V)	Tetrahydro-γ-pyrone*	67—68 (at 18 mm)	1.0844	1.4510	25.00	24.75							[6]
	Butene-2 and formaldehyde												
(VI)	4,5-Dimethyldioxane-1,3 (90%)	132.5	0.9613	1.4223	30.65	30.99	62.00	10.59		62.06	10.34		
(VII)	3-Methyl-4-hydroxytetrahydropyran (6.9%)	73 (at 6 mm)	1.0354	1.4611	30.76	30.88	62.15	10.51	14.1	62.06	10.34	14.65	
(VIII)	2-Methylbutanediol-1,3**	92 (at 6 mm)	0.9919	1.4478	28.04	28.34	57.71	11.85	31.1	57.70	11.52	32.66	
(IX)	3-Methyltetrahydro-γ-pyrone*	44—47 (at 8 mm)		1.4492									
	Isobutylene and formaldehyde												
(XI)	4,4-Dimethyldioxane-1,3 (73.35%)	132.4	0.9634	1.4238	30.99	30.79	62.42	10.47		62.06	10.34		
(XII)	2-Methylbutanediol-2,4 (7.19%)	107—109 (at 15 mm)	0.9867	1.4440	28.00	28.34							[13]
(XIII)	4,4-Dimethyl-5-hydroxymethyl-dioxane-1,3 (7.92%)	115—116 (at 11 mm)	1.0905	1.4644	36.93	37.13	57.58	9.75	11.65	57.70	9.66	11.65	

* Not obtained in the reaction products; prepared for the identification of the hydroxytetrahydropyran derivatives.

** Not found in the reaction products; prepared by methanolysis of the corresponding dioxane compounds.

TABLE 2 (continued)

Substance number	Name of compound and yield (in %)	Boiling point and pressure (in mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Found (%) C	Found (%) H	Found (%) OH	Calculated (%) C	Calculated (%) H	Calculated (%) OH	Literature data
(XV)	Triol**	150 (at 4 мм)	1.0007	1.4755	34.30	34.48	53.64	10.50		53.68	10.52		[10]
(XVI)	2-Methylbutene-2-ol-4 (0.3-1%)	139—140	0.8790	1.4389	25.73	26.35							[15]
	2-Methylbutene-2 and formaldehyde												
(XVII)	4,4,5-Trimethyldioxane (86.5%)	154.2	0.9587	1.4310	35.12	35.61	64.67	10.45		64.62	10.77		
	α-Methylstyrene and formaldehyde												
(XVIII)	4-Phenyl-4-methyldioxane (85.5%)	102 (at 4 мм)	1.0864	1.5240									[14]
	Isobutylene and acetaldehyde												
(XIX)	2,4,4,6-Tetramethyldioxane-1,3 (90.5%)	140.2	0.9039	1.4192	40.25	40.23	66.40	11.21		66.62	11.18		
(XXI)	2,4,6,6-Trimethylhydroxytetrahydropyran (2.2%)	81—83 (at 20 мм)	0.9585	1.4513	40.70	40.27	67.02	11.12		66.62	11.18		
(XX)	2-Methylpentadiol-2,4**	100—101	0.9311	1.4280	32.6	33.09	61.40	11.42		61.52	11.85		
(XXII—XXIII)	Unsaturated pyran derivatives*	137—138	0.8652	1.4390	38.40	38.36	75.91	11.32		76.14	11.18		
	Butene-2 and acetaldehyde												
(XXIV)	2,4,5,6-Tetramethyldioxane (50%)	139.5	0.9035	1.4203	40.50	40.22	66.40	11.00		66.62	11.18		

* Not obtained in the reaction products; prepared for the identification of the hydroxytetrahydropyran derivatives.

** Not found in the reaction products; prepared by methanolysis ofthe corresponding dioxane compounds.

Found %: C 57.40; H 8.72. $C_9H_{16}O_4$. Calculated %: C 57.44; H 8.57.

The reaction of a mixture of butenes with formaldehyde was carried out under conditions similar to those of Experiment 2 (Table 1). A mixture of alkyldioxanes was obtained in 88% yield: b. p. 132-135°, d_4^{20} 0.9619, n_D^{20} 1.4230.

This mixture of isomeric alkyldioxanes was decomposed catalytically in a tubular furnace over a catalyst at 425° at a volume rate of 0.63 ml/ml of catalyst per hour, diluted with steam 1 : 3 (by weight). In all, 149.6 g of dioxanes was passed through and 124.2 g was decomposed during the experiment. The catalyzate was fractionated. The total diene content of the fraction 24-50° (determined by heating a sample of the fraction with maleic anhydride at 100° for 3 hours) was 87.5% and 14.5% of butenes. The total amount of dienes was 56.3 g, (65.3% on the dioxane decomposed). The fraction was then dried carefully and distilled on a precision column, which made it possible to establish that the isoprene content of the fraction was 65% and the piperylene (trans- and cis-isomers), 35%.

Isoprene: b. p. 34.1°, d_4^{20} 0.6805, n_D^{20} 1.4220. Adduct with maleic anhydride: m. p. 63.2° (from benzine).

The piperylene fraction was collected in the range 41-44°, n_D^{20} 1.4330. The adduct with maleic anhydride: m. p. 58.5°, hydrogen number: found 670, calculated 660.

Reaction of propylene and butene-2 with acetaldehyde. These experiments were performed in ampules of ER-1T steel. Into the ampules was placed acetaldehyde (100%), the olefin (200% calculated on the acetaldehyde), a volume of dichloroethane equal to that of the olefin and $ZnCl_2$ (10% of the amount of aldehyde used).

On reacting propylene with acetaldehyde under these conditions for 6 hours, 64.7% of the aldehyde reacted. The reaction products contained a considerable amount of tar. From them we were able to isolate crotonaldehyde (b. p. 102°, n_D^{20} 1.4120) in 16% yield and 2,4,6-trimethyldioxane in 9% yield.

On reacting butene-2 with acetaldehyde under these conditions for 2 hours, 58% of the aldehyde reacted. From the reaction products we isolated crotonaldehyde (31.95%) and 2,4,5,6-tetramethyldioxane (XXIV) in 50% yield.

SUMMARY

1. We studied the reactions of the simplest olefins (propylene and butylenes) with aqueous solutions of formaldehyde and acetaldehyde in the presence of sulfuric acid.

2. It was shown that the main reaction products under these conditions were alkyldioxanes, besides a certain amount of diols and cyclic alcohols and very small amounts of unsaturated alcohols.

3. It was shown that two series of products were formed in these reactions.

4. A mechanism was put forward for the reactions examined. The formation of two series of products was explained by the capacity of olefins to react with the transfer of the reaction center.

LITERATURE CITED

[1] E. Arundale, L. Mikeska, Chem. Revs. 51, 505 (1952); Prog. Chem. 23, 223 (1954).

[2] H. Prins, Zbl. 1918, I, 168; 1919, II, 1001; 1920, I, 423.

[3] E. Fourneau, G. Benoit, R. Firmenich, Bull. Soc. Chim. 47, 860 (1930).

[4] J. Baker, J. Chem. Soc. 1944, 296.

[5] M. I. Farberov and N. K. Shemyakina, J. Gen. Chem. 26, 2749 (1956).*

[6] M. I. Farberov, E. P. Tepenitsyna and N. K. Shemyakina, Proc. Acad. Sci. USSR, 99, 793 (1954); J. Gen. Chem. 25, 133 (1955).*

[7] H. Adkins and E. Adams, J. Am. Chem. Soc. 47, 1368 (1925).

[8] S. Ballard, H. Holm, P. Williams, J. Am. Chem. Soc. 72, 5735 (1950).

* Original Russian pagination. See C. B. Translation.

[9] A. N. Nesmeyanov and M. I. Kabachnik, J. Gen. Chem. 25, 41 (1955).*

[10] S. Siggia, Quantative Organic Analysis via Functional Groups, 163 (1949).

[11] M. Bergmann, A. Mickeley, E. Lippman, Ber. 62, 1474 (1929).

[12] E. Grischkewitch-Trochimowsky, J. Chem. Soc. 112, 154 (1917).

[13] M. Davydova, Z. Papkina and D. Tishchenko, J. Gen. Chem. 7, 1942 (1937).

[14] J. Baker, J. Chem. Soc. 1948, 89.

[15] I. N. Nazarov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 419.

Received April 16, 1956

Yaroslav Institute of Technology and Experimental Plant of the Ministry of Chemical Industry

*Original Russian pagination. See C. B. Translation.

TRICHLOROPHOSPHAZOSULFONENITROARYLS AND THEIR HYDROLYSIS PRODUCTS

A. V. Kirsanov and N. G. Feshchenko

Trichlorophosphazosulfonenitroaryls are interesting as initial substances for the synthesis of trialkoxy- and triaroxyphosphazosulfonenitroaryls and, in particular, for the synthesis of N-phosphoric acids of sulfanilamides, their derivatives and also azo dyes containing the phosphazo group.

Trichlorophosphazosulfonenitroaryls have not been well known hitherto. o-, m- and p-Trichlorophosphazosulfonenitrophenyls were obtained by the action of phosphorus pentachloride on o-, m- and p-nitrobenzenesulfamides according to the system

$$NO_2C_6H_4SO_2NH_2 + PCl_5 \rightarrow 2HCl + \underset{(I)}{NO_2C_6H_4SO_2N{=}PCl_3}. \quad (1)$$

The reaction takes place quantitatively but at higher temperatures than in the case of benzenesulfamide and its homologs [1]. When the initial products used are chemically pure, completely pure trichlorophosphazo compounds are obtained which do not require further purification. All three trichlorophosphazosulfonenitrophenyls (I) are colorless, crystalline, comparatively low-melting substances which crystallize as prisms, readily soluble in benzene, more difficultly soluble in carbon tetrachloride and almost insoluble in ether and petroleum ether. At room temperature (I) react slowly with water and when boiled with water decompose into nitrobenzenesulfamides, phosphoric acid and hydrogen chloride.

The trichlorophosphazosulfonenitrophenyls of the type $NO_2C_6H_4SO_2N{=}PCl_3$, with the empirical molecular formula $C_6H_4O_4N_2SPCl_3$, obtained according to system (1) with yields of ~100.0%, are given in Table 1.

When acted on by 1 mole of anhydrous formic acid, all three substances give 80-85% yields of the diacyl chlorides of the corresponding nitrophenylsulfonamidophosphoric acids (II) according to the system

$$NO_2C_6H_4SO_2N{=}PCl_3 + HCOOH \rightarrow HCl + CO + \underset{(II)}{NO_2C_6H_4SO_2NHPOCl_2}. \quad (2)$$

The reaction takes place at room temperature (subsequent slight heating is effective) but with considerably more difficulty than in the case of trichlorophosphazosulfonearyls [2] and alkyls [3]. When the initial substances used were pure, the reaction products were absolutely pure and did not require recrystallization. (II) are colorless substances, crystallizing in the form of small cubes, melting with decomposition, readily soluble in acetone, dioxane, ethyl acetate, soluble with heating in benzene, more difficultly soluble in carbon tetrachloride and insoluble in ether and petroleum ether. (II) hydrolyze far more difficultly than (I), they change very slowly with atmospheric moisture but react readily with alcohols, amines and phenols. (II) are more stable to hydrolysis than the diacyl chlorides of arylsulfonamidophosphoric acids without electronegative substituents [2] and diacyl chlorides of alkylsulfonamidophosphoric acids [3].

Diacyl chlorides of nitrophenylsulfonamidophosphoric acids, of the type

$$NO_2C_6H_4SO_2NHPOCl_2,$$

with the empirical molecular formula $C_6H_5O_5N_2SPCl_2$, obtained according to system (2), are given in Table 2.

TABLE 1

Structure	Reaction temperature	Melting point	Found (as %)				Calc. (as %)			
			Cl	P	N	Equiv. after hydrol.	Cl	P	N	Equiv. after hydrolysis
Ortho-	135°	73—75°	31.54, 31.61	9.44, 9.50	8.36	5.01				
Meta-	135	82—84	31.34	—	—	5.04	31.56	9.19	8.29	5.00
Para-	160—170	118—119	31.59, 31.58	—	8.32	5.07, 5.07				

TABLE 2

Structure	Melting point (with decomp.)	Found		Calculated	
		Cl (as %)	Equiv. after hydrolysis to phenolphthalein	Cl (as %)	Equiv. after hydrolysis to phenolphthalein
Ortho-	149—151°	22.05, 22.15	4.07, 4.04	22.26	4.00
Meta-	145—147	22.35, 22.24	4.08, 3.98		
Para-	143—145	22.30, 22.42	4.09, 4.03		

TABLE 3

Structure	Melting point (with decomp.)	Found		Calculated	
		Cl (as %)	Equiv. after hydrolysis (to phenolphthalein)	Cl (as %)	Equiv. after hydrolysis (to phenolphthalein)
Ortho-	123—125°	11.38	2.81	11.85	3.00
Meta-	71—73	11.50	2.91, 2.86		
Para-	145—146	11.65	2.95, 2.95		

TABLE 4

Structure	Melting point (with decomp.)	Found		Calculated	
		P (as %)	Equiv.	P (as %)	Equiv.
Ortho-	188—190°	10.94	1.98	11.00	2.00
Meta-	159—161	10.83	1.94		
Para-	173—175	10.86	2.00		

By the action of formic acid in benzene solution at 80° for 1.5 hours (II) are converted with yields of 91-94% into monoacyl chlorides of nitrophenylsulfonamidophosphoric acids (III) according to the system

$$NO_2C_6H_4SO_2NHPOCl_2 + HCOOH \rightarrow CO + HCl + \underset{(III)}{NO_2C_6H_4SO_2NHPO(OH)Cl}. \quad (3)$$

(III) are colorless crystalline substances melting with decomposition, very difficultly soluble in boiling benzene, readily soluble in dioxane, insoluble in carbon tetrachloride, ether and petroleum ether.

It was not possible to obtain satisfactory yields of free nitrophenylamidophosphoric acids by hydrolyzing (III) with formic acid. (IV) was, therefore, obtained from (III) by the action of water according to the system

$$NO_2C_6H_4SO_2NHPO(OH)Cl + H_2O \rightarrow HCl + \underset{(IV)}{NO_2C_6H_4SO_2NHPO(OH)_2}. \quad (4)$$

The reaction takes place quantitatively. (IV) are colorless finely-crystalline substances, melting with decomposition and titrated to phenolphthalein as dibasic acids. (IV) are readily soluble in water, acetone and alcohol, insoluble in ether, benzene, carbon tetrachloride and petroleum ether. The para-isomer is appreciably more soluble in water and in alcohol and rather more difficultly soluble in acetone than the ortho-isomer, which is probably the result of the presence of hydrogen bonds in the ortho isomer.

Monoacyl chlorides of nitrophenylsulfonamidophosphoric acids of the type

$$NO_2C_6H_4SO_2NHPO(OH)Cl,$$

with the empirical molecular formula $C_6H_6O_6N_2PSCl$, obtained according to system (3) are given in Table 3.

Free nitrophenylamidophosphoric acids of the type $NO_2C_6H_4SO_2NHPO(OH)_2$, with the empirical molecular formula $C_6H_7O_6N_2SP$, obtained according to system (4), are given in Table 4.

When boiled with aqueous solutions of acids (IV) decompose into nitrophenylsulfamides and phosphoric acid. With alkalis (IV) give salts which are readily soluble in water.

EXPERIMENTAL

All the experiments were carried out in such a way that the reaction products and the reaction mixtures were given maximum protection from atmospheric moisture.

Preparation of trichlorophosphazonitrophenols (I). A mixture of 0.05 mole of ground nitrophenylsulfamide and 0.055 mole of phosphorus pentachloride was heated on an oil bath in a round-bottomed flask with a reflux condenser. A vigorous reaction commenced at 135° in the case of the ortho- and meta-isomers and at 160-170° with the para-isomer; this reaction was accompanied by a vigorous emission of hydrogen chloride and was fully completed after 15 minutes. To remove excess phosphorus pentachloride the reaction mixture was heated under vacuum at 150° for 10-15 minutes. When cooled to room temperature all three compounds (I) were completely crystallized, forming aggregates of prisms with a slightly yellow color. The "crude" products (quantitative yields) melted at the same point as the recrystallized products but after recrystallization they were completely colorless.

Preparation of diacyl chlorides of nitrophenylsulfonamidophosphoric acids (II). 0.02 mole of anhydrous formic acid was mixed with a solution of 0.02 mole of (I) in 25 ml of benzene. Slight heating of the reaction mixture and liberation of gases occurred initially but the reaction subsequently proceeded very slowly without external heating. The reaction mixture was, therefore, heated on an oil bath to 50° for 30 minutes after which it was allowed to stand for 24 hours at room temperature. The precipitated crystals of (II) were separated on a vacuum filter, washed with benzene and dried under vacuum.

Preparation of monoacyl chlorides of nitrophenylsulfonamidophosphoric acids (III). A mixture of 0.02 mole of (II), 30 ml of benzene and 0.02 mole of anhydrous formic acid was boiled with a reflux condenser for 1.5 hours a and was then allowed to stand for three days at room temperature to let monoacyl chloride completely crystallize. (III) was separated on a vacuum filter, washed with benzene and dried under vacuum.

Preparation of free nitrophenylsulfonamidophosphoric acids (IV). 0.01 mole of (III) was mixed in a small porcelain dish with 10 ml of water. Saponification took place fairly rapidly and all the substance passed into

solution. To remove water and hydrogen chloride the dish was placed in a vacuum desiccator over sulfuric acid and caustic potash. 5 ml of water was added to the dry residue and it was again evaporated under the same conditions. This operation was repeated 3-4 times. The yields of the free acids were qualitative. To purify (IV) they were carefully washed with ether, after which they titrated well and melted within limits of 2° (with decomp.) (IV) was a colorless finely-crystalline substance with an intensely acid taste. For the remaining properties of (I), (II) and (III) see the general section of the paper.

SUMMARY

Trichlorophosphazosulfonenitrophenyls and their hydrolysis products were prepared and described.

LITERATURE CITED

[1] A. V. Kirsanov, J. Gen. Chem. 22, 269 (1952);* Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 710.*

[2] A. V. Kirsanov and E. A. Abrazhanova, J. Gen. Chem., Symp. (II), 1048 (1953).

[3] A. V. Kirsanov and N. L. Egorova, J. Gen. Chem. 25, 1140 (1955).*

Received October 8, 1956

Institute of Organic Chemistry
Academy of Sciences Ukrainian SSR

* Original Russian pagination. See C. B. Translation.

THE NEUTRAL FORM OF A DIAZO COMPOUND

I. V. Grachev, G. G. Gusev and D. Z. Zavelsky

Of the various forms into which a diazo compound may be converted by altering the pH of the medium, the most important is that of a compound with a neutral character and free from mineral cations or anions.

The neutral form of a diazo compound was isolated by Hantzsch, Schumann, Engler and Pohl [1] by oxidizing an aqueous solution of a stable alkaline salt of a diazo compound (isodiazotate) with an equivalent amount of acid. The initially formed organic acid isomerizes into a compound with a neutral character, free from mineral ions. The same substance was obtained by the slow reaction of the isodiazotate with carbon dioxide. Enders [2] obtained a similar form of a diazo compound by alkalization of a diazonium salt with 1 equiv. of alkali or by treatment of the salt with sodium acetate or bicarbonate.

In the majority of the investigated (about 15) variously substituted diazo compounds, the neutral form was unstable and rapidly decomposed with the liberation of nitrous acid. Only in two instances – 1 diazo-2,6-dibromoanisole and 1-diazo-2,4,6-tribromobenzene – did Hantzsch and Pohl succeed in obtaining comparatively stable products and determining their bromine and nitrogen contents; the latter were found to be fairly close to the theoretical if the formula of the corresponding primary arylnitrosamine is assumed for the neutral diazo compound.

Later, however, Orton pointed out Hantzsch's error regarding neutral 1-diazo-2,4,6-tribromobenzene which in actual fact was an internal diazo oxide, formed by the splitting off of one atom of bromine in the ortho position to the diazo group.

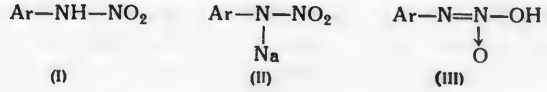
In order to avoid Hantzsch's error, Enders selected a diazo compound which did not contain a halogen or nitro group in the ortho position to the diazo group; in the case of 3,4,5-trichloro and 3,5-dichloro-4-bromodiazobenzene he succeeded in obtaining and investigating neutral yellow products, free from mineral ions and an internal diazo oxide. An analysis of the halogen in both products by the Carius method showed the agreement of the data obtained with the calculated values based on the formula of a primary arylnitrosamine. Unlike Hantzsch, Enders obtained neutral yellow products in a purer state and established that they are extremely unstable; they explode on the slightest heating and rapidly decompose in an aqueous medium, in organic solvents and when kept for a short period in the dry state. When placed in an organic solvent, the yellow substance forms a hydrocarbon (trichlorobenzene, trichlorodiphenyl) and an oxyazo compound (hexachlorooxyazobenzene) with the liberation of nitrogen. In an aqueous medium the substance forms a diazo compound with the splitting off of nitrous acid, especially smoothly in the presence of sulfaminic acid.

From the above it follows that only in isolated instances was it possible to separate, analyze and investigate the unstable neutral form of a diazo compound assumed by Hantzsch, Pohl and Enders and others to be a primary arylnitrosamine. Nevertheless, the individual data obtained were quite adequate to add confirmation of this false assumption. Until now the majority of textbooks on organic chemistry and manuals for the course on dyestuffs and intermediates have included the false conception of Hantzsch and others who saw the neutral form of a diazo compound as a primary arylnitrosamine. For example, Hantzsch's system, in which primary arylnitrosamine occupies one of the central positions as a neutral form of a diazo compound, is referred to without substantial

modification or reservation in N. N. Vorozhtsov's well-known book [4].*

Hantzsch and other investigators consider primary arylnitrosamines or arylnitramines to be neutral compounds and pseudo-acids. From the theoretical point of view this assumption is incorrect. It is necessary to take into consideration the acidifying influence of an aryl radical next to the hydrogen of an imino group, on the one hand, and, in particular, of a nitroso or nitro groups, on the other hand. This being the case, primary arylnitrosamines or arylnitramines cannot be neutral compounds but are true acids (nitrosaminic or nitraminic acids).

Fairly recently it was possible to confirm this hypothesis experimentally in a very definite manner in the case of primary arylnitramines [7]. The conversions, titrated curves and spectra (infra-red and Raman) of a primary arylnitramine, its sodium salt and oxodiazohydrate were studied.

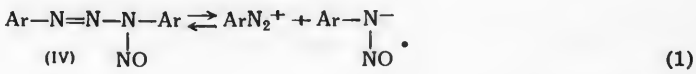


(I) (II) (III)

The data obtained were in direct contradiction to current ideas. For example, it was established that a primary arylnitramine (I) is not a neutral compound but a true acid equal in strength to correspondingly substituted benzoic acid. In an alkaline medium an arylnitramine gives a sodium salt which has a nitramine structure (II) and not an "aci-" structure. In an acid medium an arylnitramine isomerizes reversibly into an oxodiazohydrate (III), with the properties of a fairly strong base, not those of an acid, as was assumed by Hantzsch and many others. The term "aci-form of nitramine" is, therefore, quite unsuitable.

Similar physico-chemical and physical investigations of a primary arylnitrosamine have, unfortunately, not yet proven possible because of the extreme instability of this compound. The nitrosamine structure of the stable alkaline salt of a diazo compound (isodiazotate) was, however, fairly convincingly shown by the works of a number of authors [8].

The actual structure of the neutral form of a diazo compound was established by one of us [9] for the first time by studying the conversions of a diazo compound, principally p-nitrodiazobenzene, at various values of the pH medium of aqueous solutions, using a glass electrode. The investigations carried out showed that the neutral form of a diazo compound is a diaryl-N-nitrosotriazene (diazonitrosaminate) (IV), readily dissociating in aqueous solution into a diazo cation and nitrosaminate anion:



(IV) (1)

Its reaction with mineral acid or with an azo component are in agreement with the above-mentioned dissociation of diaryl-N-nitrosotriazene. For example, when the experiment is carried out rapidly, 1 mole of HCl or 1 mole of azo component is consumed in the titration with N-nitrosotriazene, whereas if the experiment is carried out fairly slowly (1-2 hours), the N-nitrotriazene enters the reaction with 2 molecules of HCl or with

* At the same time a further incorrect assumption in N. N. Vorozhtsov's book must be mentioned; this concerns the structure of the alkaline salts of a diazo compound. In agreement with Hantzsch's representations, N. N. Vorozhtsov Jr. considers that there are two anions of a diazo compound, with a syn- and an anti-structure. At the same time, the assumption made by I. V. Grachev and B. A. Porai-Koshits [5], and also by Hodgson and Marsden [6], that there exist two different anions of a diazo compound, having a diazo and a nitrosamine structure, was rejected on the grounds that in this instance there must be one common conjugated anion of the diazo compound and that, therefore, one alkaline, for example, sodium salt of the diazo compound must exist, Leaving aside this complicated problem which requires additional experimental data, the assumption of a syn- and anti-structure of a diazo compound's anions must be rejected on the following grounds. Taking note of the acid character of a primary arylnitrosamine it would be possible to conclude that there are three different anions (syn-, anti- and nitrosamine – in the conjugated state, of course, and by no means identical with syn- or anti-anions). In this instance, therefore, there would necessarily be three, for example, sodium salts of a diazo compound; this is inconsistent with the known facts.

2 moles of azo component since in the course of time the nonactive form (nitrosaminate ion) passes completely into the active form (diazo cation).

In confirmation of Enders' data it was shown that the neutral form of a diazo compound decomposes rapidly and easily in an aqueous solution with the formation of a diazoamino compound and nitrous acid. This reaction is most simply explained by the hydrolysis of N-nitrosotriazene

$$Ar{-}N{=}N{-}\underset{\displaystyle NO}{\underset{|}{N}}{-}Ar + \underset{\displaystyle OH}{\underset{|}{H}} \rightleftarrows Ar{-}N{=}N{-}NH{-}Ar + HONO \qquad (2)$$

Since the dissociation of N-nitrosotriazene into ions (1) is reversible, it could be assumed that this compound must be formed from a diazo cation and a nitrosaminate anion. In actual fact it was found that the neutral form of a diazo compound may be readily obtained by mixing equimolecular solutions of the diazonium chloride and the sodium salt of nitrosaminic acid (isodiazotate). A universal method of obtaining the neutral form of a diazo compound with various substituents in one or both aromatic rings was, therefore, found.

As already mentioned above, the neutral form of a diazo compound is obtained by two other methods: by acidifying the isodiazotate with an equivalent amount of acid followed by spontaneous conversion of the nitrosaminic acid into N-nitrosotriazene, or by alkalization of the diazonium salt with an equivalent amount of alkali followed by spontaneous conversion of the diazo oxide (hydrolyzed to a considerable extent to diazohydrate) into the same triazene

$$\begin{array}{l} Ar{-}\underset{\displaystyle Na}{\underset{|}{N}}{-}NO \xrightarrow{H^{\oplus}} Ar{-}NH{-}NO \\ ArN_2^{\oplus}Cl^{\ominus} \xrightarrow{OH^{\ominus}} \underset{(Ar\bar{N}{=}N{-}O\bar{H})}{ArN_2{-}O{-}N_2Ar} \end{array} \longrightarrow Ar{-}N{=}N{-}\underset{\displaystyle NO}{\underset{|}{N}}{-}Ar \qquad (3)$$

The last two methods of obtaining the neutral form of a diazo compound have a number of disadvantages compared with the first: the restricted application (only for nitro- or polyhaloid substituted diazo compounds), the fact that only N-nitrosotriazenes which are symmetrically substituted in both aromatic rings can be obtained, and, finally, the low degree of purity of the products obtained, this being associated with the duration of the process of spontaneous conversion into N-nitrosotriazene and with the instability of the latter.

The above-mentioned investigations by one of us had a serious disadvantage. They were carried out exclusively in aqueous solutions, without isolating the diaryl-N-nitrosotriazene in the solid state, a fact which did not favor a complete and convincing proof of the structure of this compound.

Later, by reacting a diazonium salt with a primary arylnitramine or sulfaminic acid, its derivatives, N-nitrotriazenes (V) and N-sulfotriazones (VI) [10] were obtained, which were very similar, as regards structure and properties, to N-nitrosotriazenes (IV).

$$\underset{\displaystyle NO}{\underset{|}{R{-}N{=}N{-}N}}{-}R_1 \quad (V) \qquad\qquad \underset{\displaystyle SO_3H}{\underset{|}{R{-}N{=}N{-}N}}{-}R_1 \quad (VI)$$

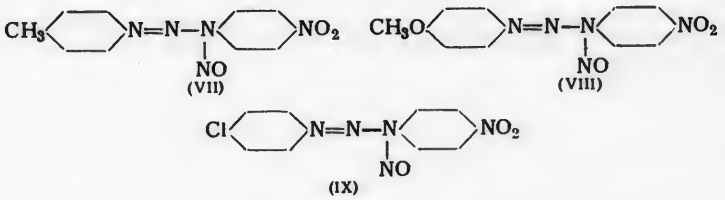
Using the experience accumulated from investigations on a series of N-substituted triazenes, we set ourselves the task of obtaining and isolating a diaryl-N-nitrosotriazene in a solid and reasonably pure state for purposes of analysis and the subsequent investigation of its properties. We hoped to be able to obtain new data to prove the actual structure of the neutral form of a diazo compound and correct existing false ideas on this subject.

About 20 different diaryl-N-nitrosotriazenes were obtained by condensing the phenylnitrosaminate, and also sodium p-nitrophenyl- and o-chloro-p-nitrophenylnitrosaminates with diazonium chlorides. As would be

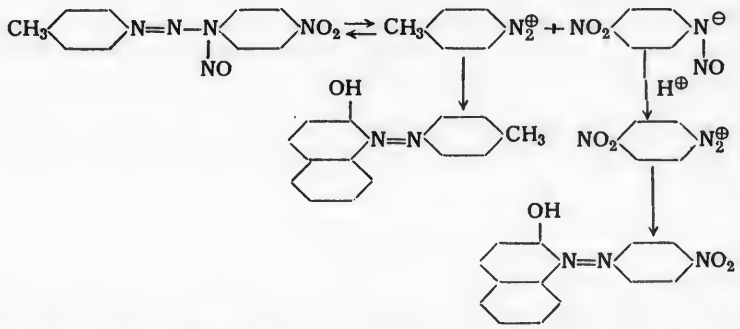
expected, when the diazonium salts used had positive substituents, the diaryl-N-nitrosotriazenes obtained were found to be comparatively stable on keeping and sufficiently pure to carry out investigations and analyses. All the products obtained decomposed when dissolved in organic solvents and they, therefore, could not be purified by recrystallization or their molecular weights determined.*

The proof of the fact that two, and not one, aromatic radicals are included in the molecule of the neutral form of a diazo compound was obtained by means of reactions of hydrolysis and azo coupling.

The azo coupling of three representatives of N-nitrosotriazenes (VII, VIII and IX) with β-naphthol



was carried out in an aqueous-caustic soda medium and after preliminary separation of the dye and acidification in a bicarbonate medium. When coupled in a medium of caustic soda only the diazo cation took part in the reaction and the nitrosaminate ion remained unchanged. After the dye has been separated and acidification carried out, the nitrosaminic acid which remained isomerized into the diazonium compound which, by entering the azo coupling reaction with β-naphthol, formed an azo compound with a structure different from the azo compound first isolated.

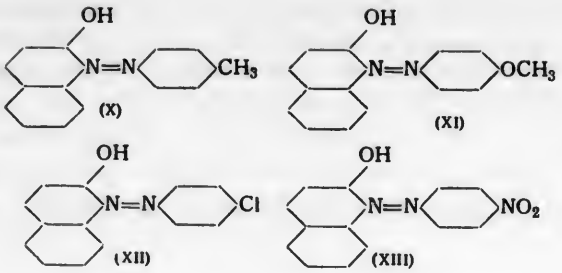


A quantitative determination showed that in a medium of caustic alkali 1 mole of β-naphthol is consumed per mole of N-nitrosotriazene, and after acidifying and coupling in a bicarbonate medium another 1 mole of β-naphthol is consumed.

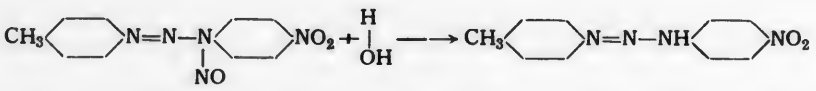
The dyes obtained by coupling N-nitrosotriazenes with β-naphthol were recrystallized from glacial acetic acid and were identified by their melting points with known azo compounds obtained.

It was found that the azo compounds (X), (XI) and (XII) are obtained by coupling in a medium of caustic soda. After the separation of these dyes, acidification and coupling in a bicarbonate medium, the same azo compound (XIII) is formed in the case of all three N-nitrosotriazenes.

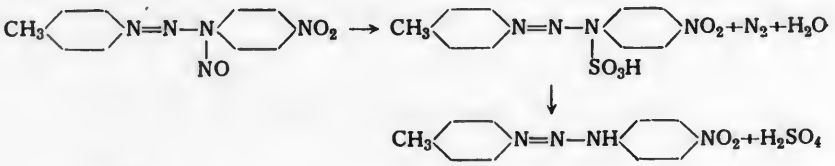
* If it had been possible to determine the molecular weight and to determine the moisture content of the neutral compounds obtained by Hantzsch, Pohl and Enders, it would naturally have been possible to make a more correct selection between the formula ArN_2OH and the double formula $Ar_2N_4O \cdot H_2O$.



When 4-tolyl-4'-nitrophenyl-N-nitrosotriazene is hydrolyzed, nitrous acid is split off and 4-methyl-4'-nitrodiazoaminobenzene is formed.



The hydrolysis of N-nitrosotriazene in the presence of sulfaminic acid is accompanied by the intermediate formation of a water-soluble product. It may be assumed that in this process a water-soluble unstable N-sulfotriazene is formed.



The structure of 4-tolyl-4'-nitrophenyl-N-nitrosotriazene was confirmed by the data of determinations of the moisture and diazo nitrogen contents and also by data from the ultimate analysis for carbon, hydrogen and nitrogen by combustion.

EXPERIMENTAL

Preparation of N-nitrosotriazenes. Equimolecular amounts of aqueous solutions (0.01-0.005 mole) of sodium or potassium nitrosaminate (isodiazotate) and diazonium chloride were mixed together and stirred at 0-3° in the presence of sodium bicarbonate. If sufficiently stable, the finely-crystalline yellow precipitate of N-nitrosotriazene formed by this process was filtered, washed with ice water and with ether and dried in a darkened desiccator over solid alkali.

In the condensation of phenylnitrosaminate with diazotized aniline, p-anisidine, anthranilic acid, 2,5-dichloro-p-nitro- or o-chloro-p-nitroaniline, the yellow precipitate which is immediately formed decomposes almost at once in the reaction medium with the evolution of gas (nitrogen, nitrous acid) and is converted into a bubbly, viscous and sticky dark brown tar.

When 2-chloro-4-nitrophenylnitrosaminate is condensed with diazotized p-nitroaniline or with bisdiazodiphenyl, the same unstable products are obtained, which decompose almost immediately after formation with evolution of gas and conversion into a dark tar.

When the same nitrosaminate is condensed with diazotized p-anisidine or m- or p-toluidine, however, the N-nitrosotriazene obtained can be filtered, dried and kept without any visible change in the dry state for a period of no more than 1 hour.

When p-nitrophenylnitrosaminate is condensed with diazotized 2,5-dichloro-, p-nitro or m-nitroanilines or with bisdiazophenyl, unstable N-nitrosotriazenes are obtained. When the same nitrosaminate is condensed with diazotized aniline and, in particular, with anthranilic acid, p-chloroaniline, p-anisidine, p-toluidine and m-xylidine, comparatively stable N-nitrosotriazenes are obtained; these can be kept in the dry state for several hours without visible change.

General properties of N-nitrosotriazenes. Dry N-nitrosotriazene explodes with friction on percussion or slight heating. With intense and rapid heating it deflagrates. 4-Chlorophenyl-4'-nitrophenyl- and 2-carboxy-phenyl-4'-nitrophenyl-N-nitrosotriazenes are particularly sensitive to external shocks. N-Nitrosotriazene gives a characteristic color for diazoamino compounds with a solution of α-naphthylamine in glacial acetic acid. The splitting-off of this triazene also takes place, however, in the absence of acid in an alcoholic or aqueous medium. For example, with β-naphthol a red dye is formed both in an alcoholic and an aqueous medium (within a wide range of pH values). In water there is a neutral reaction but in time the compound decomposes, showing a definite reaction for free diazo cation (test with a solution of R-salt), an acid reaction to litmus and the presence of nitrous acid (test with starch-iodide paper). It shows a negative reaction for the chlorine ion (test with a silver nitrate solution) and does not contain the sodium ion either (absence of ash from the combustion of the substance moistened and wetted with sulfuric acid). It dissolves in the majority of organic solvents with an intense evolution of nitrogen. It dissolves, sometimes with an explosion, in tertiary organic bases (pyridine, triethylamine). It dissolves without an appreciable evolution of gas in aniline, xylidine and other aromatic amines (evidently with complete splitting-up of the N-nitrosotriazene into its components). When kept in the dry state, particularly in light, it decomposes with evolution of gas (nitrogen, nitrous acid) and is converted into a dark brown, sometimes black tar. The rate of decomposition of the N-nitrosotriazene depends on the character of the substituents it contains. N-Nitrosotriazene containing negative substituents (NO_2 group, etc.) in the diazonium ring decomposes particularly rapidly but, on the other hand, the most stable product is obtained in the case of diazonium containing positive substituents (CH_3, OCH_3, etc.)

4-Tolyl-4'-nitrophenyl-N-nitrosotriazene. a) Determination of the moisture content. A weighed sample of aniline (40-50 g) was placed in a 150 ml long-necked, round-bottomed flask, the side arm of which was packed with finely ground calcium hydride powder (1-2 g). After the air had been removed from the system by passing a current of dry carbon dioxide, the calcium chloride powder was added. The liberated hydrogen was collected in an azotometer over a 28% solution of caustic potash. The last stage of the reaction was carried out at 70-80°. The experiment with a solution of nitrosotriazene in aniline was carried out similarly. The moisture content was determined by the difference between the values of the hydrogen volumes found, with a correction for the nitrogen liberated as a result of decomposition. For this purpose the azotometer containing the mixture of hydrogen and nitrogen was connected to a quartz tube filled with cupric oxide, the hydrogen was burned and the volume of unburned nitrogen was measured. In addition to combustion of the hydrogen its volume was determined from data of the specific gravity of a mixture of hydrogen and nitrogen.

Found %: H_2O 5.80, 5.19. $C_{13}H_{11}O_3N_5 \cdot H_2O$. Calculated %: H_2O 5.94.

b) Determination of the diazo nitrogen. External cooling was employed when the air was expelled from the system in order to avoid decomposition of the N-nitrosotriazene. After 50 ml of 50% sulfuric acid had been added, the solution was heated to boiling and the nitrogen was collected in an azotometer over 40% caustic potash.

Found %: N 18.55, 18.51. $C_{13}H_{11}O_3N_5 \cdot H_2O$. Calculated %: N 18.45.

c) Ultimate analysis of C, H and N by combustion. In view of the extreme instability and explosibility of N-nitrosotriazene, the ultimate analysis for C and H was carried out in a copper combustion boat, about 18-20 cm long, specially prepared for this purpose. The weighed sample of triazene was distributed in small quantities along the length of the boat between small heaps of fine cupric oxide powder. Each separate quantity of triazene was carefully heated in turn and the whole product was thus gradually decomposed and burned. The determination of the nitrogen was carried out on a microsample with a considerable amount of carefully mixed fine cupric oxide powder.

Found %: C 51.23, 51.10; H 4.22, 4.08; N 23.46, 22.89. $C_{13}H_{11}O_3N_5 \cdot H_2O$. Calculated %: C 51.48; H 4.32; N 23.09.

d) Coupling with β-naphthol in an acid medium. A weighed sample of N-nitrosotriazene was dissolved in 10-15 ml of glacial acetic acid and an excess of 0.05 N solution of β-naphthol was added to the solution. The pH value of the solution was brought up to 7 by the gradual addition of sodium bicarbonate with continuous stirring, and the solution was then left for 25-30 minutes. A small amount of alkali was then added, and the solution was stirred for a further 15 minutes and the excess β-naphthol remaining was back-titrated with a 0.05 N solution of phenyldiazonium.

Found: the consumption of β-naphthol per mole of N-nitrosotriazene was 1.92, 1.86.

e) Coupling with β-naphthol in a weakly-alkaline medium. An excess of a 0.05 N solution of β-naphthol was added to a weighed sample of the triazene suspended in 20-25 ml of a saturated solution of sodium bicarbonate. After it had been left for 15-20 minutes, the remaining β-naphthol was back-titrated with a 0.05 N solution of phenyldiazonium.

Found: the consumption of β-naphthol per mole of N-nitrosotriazene was 0.85, 0.83.

f) Preparation of p-tolueneazo-β-naphthol and p-nitrobenzeneazo-β-naphthol. The dye obtained by mixing N-nitrosotriazene and β-naphthol (slight excess) for 20 minutes in the presence of bicarbonate or alkali was filtered, washed with a solution of alkali and with water, then dried and recrystallized from glacial acetic acid. After the removal of the first dye the weakly-alkaline filtrate, together with the wash water, was acidified with hydrochloric acid and bicarbonate was then added again (until a neutral reaction was obtained) as well as a solution of β-naphtholate. After filtration the dye obtained was washed and dried and then recrystallized from glacial acetic acid.

The first dye had an m. p. of 129.5-130°, which corresponds, according to literature data (m. p. 130°), to the azo compound obtained from β-naphthol and p-diazotoluene [11]. A mixed melt of the dye and known toluene-(4-azo-1)-2-naphthol, with an m. p. of 130-131° did not show an appreciable depression of the melting point (129.5-130.5°).

The second dye had an m. p. of 248.5-250°, which corresponds, according to data [11], to the azo compound obtained from p-nitrodiazobenzene and β-naphthol (m. p. 250°). A mixed melt of the dye and known 4-nitrobenzene-(1-azo-1)-2-naphthol had an m. p. of 249.0-251.0°.

g) Hydrolysis to 4-tolyl-4'-nitrophenyltriazene and nitrous acid. Like all compounds of this class, 4-tolyl-4'-nitrophenyl-N-nitrosotriazene has a neutral reaction in water. On standing, the reaction of the aqueous medium becomes slightly acid to litmus, nitrous acid can be detected (blue color with starch-iodide paper) and a free diazo compound is formed (test with a solution of R-salt). The precipitate which darkens after filtration no longer forms a dye with an alcoholic solution of β-naphthol, gives a red color with a solution of α-naphthylamine in glacial acetic acid, loses its explosive properties and has a high melting point, i.e., its properties correspond to those of a diazoamino compound. The diazoamino compound can easily be isolated in the pure form by carrying out the reaction in the presence of sulfaminic acid.

Sulfaminic acid (3 moles per mole of triazene) was added to a weighed sample of freshly prepared N-nitrosotriazene suspended in water. After it had been stirred for 2-3 hours the bulk of the precipitate passed into solution with an intense evolution of nitrogen. A golden-yellow precipitate (yield 50%) was gradually deposited over a period of 2-3 days from the solution filtered from insoluble tarry admixtures. After it had been recrystallized twice from alcohol, the precipitate had an m. p. of 155-157.5°. According to data [12], 4'-nitro-4-methyldiazoaminobenzene has m. p. of 158.5-161.5°. A mixed melt with known 4'-nitro-4-methyldiazoaminobenzene (156.5-158°) showed no depression of the melting point (154.5-157°).

The formation of p-anisoleazo-β-naphthol and p-nitrobenzeneazo-β-naphthol from 4-anisyl-4-nitrophenyl-N-nitrosotriazene. Freshly prepared 4-anisyl-4'-nitrophenyl-N-nitrosotriazene was added to a solution of β-naphthol in caustic soda and after stirring for 10-15 minutes at room temperature the dye formed was filtered and washed. The filtrate was acidified with hydrochloric acid and the pH of the medium was gradually brought up to 7 by the gradual addition of bicarbonate. The second dye formed with β-naphthol was filtered, washed and dried. Both dyes were recrystallized twice from glacial acetic acid.

The first dye had an m. p. of 139-140°, which corresponds, according to data [11], to anisole-(4-azo-1)-2-naphthol (m. p. 139°). The second dye with an m. p. of 249-250.5° corresponds to 4-nitrobenzene-(1-azo-1)-2-naphthol, with an m. p. of 250° [11]. Mixed melts of both dyes with the corresponding azo compounds obtained

from β-naphthol and diazoanisole (m. p. 139-139.5°), β-naphthol and diazo-p-nitrobenzene (m. p. 250-251.5°), showed no appreciable depression of the melting point.

The formation of p-chlorobenzeneazo-β-naphthol and p-nitrobenzeneazo-β-naphthol from 4-chlorophenyl-4'-nitrophenyl-N-nitrosotriazene. After acidification in a bicarbonate medium (see above), two dyes were obtained from 4-chlorophenyl-4'-nitrophenyl-N-nitrosotriazene by coupling in a medium of caustic soda; the dyes were recrystallized from glacial acetic acid.

The first dye had an m. p. of 159.5-163°, the m. p. of the second was 248.5-250.5°. According to data [11], the azo dye obtained from β-naphthol and p-chlorodiazobenzene has an m. p. of 160° while that from β-naphthol and p-nitrodiazobenzene has an m. p. of 250° [11]. A mixed melt of the first dye with known 4-chlorobenzene-(1-azo-1)-2-naphthol (160-161.5°) showed no appreciable depression of the melting point (158.5-162°). A mixed melt of the second dye with known 4-nitrobenzene-(1-azo-1)-2-naphthol (250-251.5°) also showed no depression of the melting point.

SUMMARY

1. 4-Tolyl-, 4-anisyl-, 4-chlorophenyl-4'-nitrophenyl-N-nitrosotriazenes and other diaryl-N-nitrosotriazenes were obtained in a crystalline state by condensing sodium 4-nitrophenylnitrosaminate with 4-tolyl-, 4-anisyl-, 4-chlorophenyldiazonium chlorides, etc. The 4-tolyl-4'-nitrophenyl-N-nitrosotriazene was analyzed, some of its properties were studied and the structure of diaryl-N-nitrosotriazenes was established.

2. In an aqueous or alcoholic medium diaryl-N-nitrosotriazenes dissociate into a diazonium cation and a nitrosaminate anion and are readily hydrolyzed, splitting off nitrous acid with the formation of the corresponding diazoaminobenzene.

3. Diaryl-N-nitrosotriazenes are neutral diazo compounds, capable of undergoing an azo coupling reaction in an aqueous, alcoholic or other medium. Only the diazonium part of the N-nitrosotriazene takes part in the azo coupling reaction in a neutral aqueous medium. After preliminary acidification both parts of the molecule take part in the azo coupling reaction.

4. The new data obtained confirm the erroneous nature of the widely held opinion that the neutral form of a diazonium compound is a primary arylnitrosamine.

LITERATURE CITED

[1] A. Hantzsch, M. Schumann, A. Engler, Ber. 32, 1711 (1899); A. Engler, Ber. 33, 2188 (1900); A. Hantzsch, W. Pohl, Ber. 35, 2978 (1902).

[2] G. Enders. Diss.: "Über Diazoverbindungen und die primären Arylnitrosamine." Leipzig (1934).

[3] Orton, J. Chem. Soc. 83, 796 (1903).

[4] N. N. Vorozhtsov. Bases of the Synthesis of Intermediates and Dyes [In Russian]. GNTI, Chem. Lit. 440 (1955).

[5] I. V. Grachev, B. A. Porai-Koshits, J. Gen. Chem. 16, 571 (1946).

[6] H. H. Hodgson, E. Marsden, J. Chem. Soc. 1945, 207.

[7] G. S. Salyamon, I. V. Grachev, B. A. Porai-Koshits, J. Gen. Chem., Symp., II, 1315, 1337 (1953); G. S. Salyamon, N. G. Yaroslavsky, ibid, 1325; G. S. Salyamon, Ya. S. Bobovich, ibid, 1332.

[8] C. Schraube, C. Schmidt, Ber. 27, 514 (1894); E. Bamberger, Ber. 27, 679, 914 (1894); H. v. Pechmann, Ber. 25, 3505 (1892); A. Wohl, Ber. 25, 3631 (1892); H. v. Pechmann, L. Frobenius, Ber. 27, 672 (1894); E. Bamberger, J. Müller, Lieb. Ann. 313, 97 (1900); E. Bamberger, O. Baudisch, Ber. 42, 3568 (1909).

[9] I. V. Grachev, J. Gen. Chem. 17, 2268 (1947); 18, 838 (1948); I. V. Grachev, N. A. Kirzner, J. Gen. Chem. 18, 1525 (1948); 19, 1335 (1949).*

* Original Russian pagination. See C. B. Translation.

[10] N. M. Baranchik, I. V. Grachev, D. Z. Zavelsky, Proc. Acad. Sci. USSR, 89, 1007 (1953); 94, 701 (1954); J. Gen. Chem. 23, 1572 (1953); D. Z. Zavelsky, L. L. Lishnevskaya, J. Gen. Chem., Symp. I, 434, 446 (1953); J. Gen. Chem. 25, 362 (1955);* D. Z. Zavelsky, Symp. in memory of A. E. Porai-Koshits; State Chem. Press, 271 (1949).

[11] A. Brunner, The Analysis of Azo Dyes [In Russian]. State Chem. Press, 92, 94 (1933).

[12] E. Bamberger, Ber. 28, 839 (1895).

Received October 24, 1956

*Original Russian pagination. See C. B. Translation.

THE REACTION OF A HYDROCHLORIC-ACID SOLUTION OF IODINE TRICHLORIDE WITH CERTAIN UNSATURATED COMPOUNDS

Ya. A. Fialkov and F. E. Kagan

Many works [1-10] have been devoted to the reaction of iodine chloride with unsaturated compounds. Similar reactions with iodine trichloride have been far less studied. A. N. Nesmeyanov and R. Kh. Freidlina [11] showed that when a hydrochloric-acid solution of ICl_3 reacts with acetylene, chlorovinyliodinetrichloride $ClCH=CHICl_2$ is formed; substances which can combine with ICl_3 to form a complex (hydrochloric acid solutions of potassium chloride, pyridine hydrochloride), however, free acetylene from this compound. E. M. Brainina and R. Kh. Freidlina [12] added ICl_3 to acetylenedicarboxylic acid, the dimethyl ester of acetylenecarboxylic acid and fumaric acid. They obtained β-chloro-substituted iodoso salts. The reactions were carried out with solutions of ICl_3 in an aqueous solution of sodium chloride.

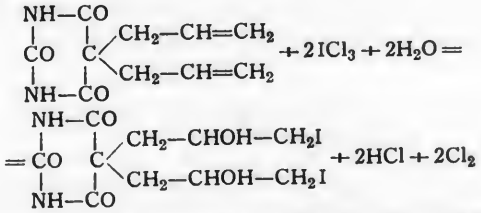
We studied the reaction of a number of unsaturated compounds containing one double bond with hydrochloric-acid solutions of ICl_3. For purposes of comparison the reactions of these compounds with iodine chloride were also studied. The materials used were representatives of various classes of organic compounds: hydrocarbons (styrene, stilbene), diallylbarbituric acid (dial), containing two allyl radicals, unsaturated acids with a double bond in various positions (cinnamic, petroselinic, oleic) and the esters of certain acids (the ethyl esters of cinnamic and petroselinic acids). The reaction products of hydrochloric acid solutions of ICl_3 and ICl with the above-mentioned compounds were isolated and the presence of chlorine and iodine in them was determined. These experiments showed that in their reactions with these unsaturated compounds ICl_3 and ICl form the same products (see Table 1). On the basis of this we came to the conclusion that in these reactions iodine trichloride decomposes with evolution of chlorine, leading to the formation of ICl which enters the reaction, for example, as follows:

$$C_6H_5CH=CH_2 + ICl_3 = C_6H_5CHCl-CH_2I + Cl_2.$$

The decomposition of ICl_3 into ICl and chlorine is in agreement with the behavior of iodine trichloride in substitution reactions where, as we have earlier shown, chlorine is also liberated [13]. The liberation of chlorine as a result of the reaction of ICl_3 with dial was proved by us by the investigation of the filtrate after the reaction products had been separated.

The reaction products of dial and cinnamic acid contained only iodine but the other compounds, however, add both iodine and chlorine at the double bond.

The melting points of the iodo derivatives of dial and cinnamic acid corresponded to the values given in literature for dial iodohydrin and iodohydroxycinnamic acid. The data obtained make it possible to draw the conclusion that the reaction proceeds according to the following equations.



$$C_6H_5CH=CH-COOH + ICl_3 + H_2O = C_6H_5CHOH-CHI-COOH + HCl + Cl_2$$

The liberation of 2 equiv. of HCl in the reaction with dial, and 1 equiv. of HCl in that with cinnamic acid, was proved by titrating the reaction mixture with alkali after the separation of the iodized product.

TABLE 1

Reaction products	External appearance	Melting point	
		of the isolated substance	according to literature data
Iodochlorostyrene	Colorless crystals	39-41°	46°
Iodochlorostilbene	Colorless crystals	131	131
Dial iodohydrin*	Yellowish crystals	213-215 (decomp.)	215 (decomp.)
Iodohydroxycinnamic acid**	Colorless crystals	141-141.5	141
Iodochloropetroselinic acid	Greasy liquid	–	–
Iodochlorooleic acid	Oily liquid	–	–
Ethyl ester of iodochloropetroselinic acid	Colorless crystals	–	–
Ethyl ester of iodochlorocinnamic acid	Colorless crystals	70-71	71

*The reaction product of dial with iodine chloride was studied by Ya. A. Fialkov and L. I. Rapoport [14].
**The reaction product of cinnamic acid and iodine chloride was studied by Erlenmeyer [6].

The results of our experiments confirm the data [6, 14] that when unsaturated organic compounds react with iodine chloride, iodohydrins are obtained only when a lactone can be formed as an intermediate product, as, for example, with dial and cinnamic acid.

The experiments carried out also showed that the conversion of the unsaturated acid to ester does not always equally reflect the capacity for the addition of halogens. In petroselinic acid, where the carboxylic group is at some distance from the double bond, the introduction of an ethyl radical does not influence the capacity of the double bond to add halogens. In cinnamic acid with a double bond in the α-position to the carboxylic group, the introduction of an ethyl radical reduces the capacity to add halogens. Cinnamic acid reacts quantitatively with hydrochloric acid solutions of ICl and ICl_3 with the formation of iodohydrin; under similar conditions ethyl cinnamate forms an iodochloro derivative, the addition reaction of iodine chloride from the hydrochloric acid solution taking place very slowly and not quantitatively.

EXPERIMENTAL

Study of the reaction of a hydrochloric acid solution of iodine trichloride with diallylbarbituric acid (dial). a) Separation and analysis of the precipitate. A weighed sample of dial (0.3 g) was dissolved in 100 ml of hot water; after it had cooled, an excess of a 0.1 N solution of ICl_3 was added and the mixture was left for 1 hour. The crystalline precipitate formed was filtered, washed first with hydrochloric acid to remove the excess ICl_3 and then with water until the wash water gave a negative reaction for chlorine. The precipitate was dried at 100°. The iodine content was determined by Stepanov's method, followed by titration with a solution of $AgNO_3$ in the presence of an external indicator, starch-nitroso paper.

Found %: I 51.19, 51.30. $C_{10}H_{14}O_5N_2I_2$. Calculated %: I 51.19.

b) Analysis of the filtrate. After the iodized dial had been separated and the excess ICl_3 decomposed with potassium iodide, the acid content in the filtrate was determined by titrating with a 1 N solution of caustic soda in the presence of methyl orange. The amount of HCl liberated by the reaction of ICl_3 with dial was calculated from the difference between the known acidity of the ICl_3 solution and the amount of acid used for washing the precipitate.

The weight of the sample of dial was 0.3024, 0.1020 g. The amount of HCl liberated (in milliliters of 1 N solution) was 2.89, 0.88, (in moles per mole of dial) 1.99, 1.79.

Study of the reaction of hydrochloric acid solutions of ICl_3 and ICl with cinnamic acid. About 0.3 g of cinnamic acid was dissolved in 100 ml of hot water and 150-200 ml of a 0.1 N solution of ICl or ICl_3 was added

to the solution cooled to 30-40°. After 1 hour a solution of potassium iodide was added to decompose the excess ICl or ICl_3 and the liberated iodine was combined with a 1 N solution of $Na_2S_2O_3$. The reaction product of cinnamic acid and ICl or ICl_3 was extracted from the solution with ether. The ether was evaporated off and the residue was recrystallized from hot benzene. In some experiments the extraction of the reaction product was carried out with hot chloroform until the excess ICl_3 was decomposed with potassium iodide.* Analysis showed that in all the experiments the same reaction product – β-phenyl-β-hydroxy-α-iodopropionic acid – was obtained. The halogen content in the crystals obtained was determined by Stepanov's method, the presence of iodine and the absence of chlorine being established.

Found %: I 43.40, 43.24. $C_9H_9O_3I$. Calculated %: I 43.47.

Formation and analysis of iodochlorostyrene and iodochlorostilbene. A weighed sample of styrene was dissolved in alcohol, a weighed sample of stilbene was dissolved in ether and an excess of a 0.1 N solution of ICl or ICl_3 was added. The precipitates formed were separated and washed with hydrochloric acid and water; after they had been dried over sulfuric acid the iodochlorostyrene was recrystallized from alcohol and the iodochlorostilbene from benzene.

Low results were obtained in the determination of the halogens in compounds, containing iodine and chlorine, by Stepanov's method; in compounds of this type we therefore determined the total halogen content by the Carius method.

Iodochlorostyrene. 6.820, 10.130 mg of the substance. Found (mg): AgCl + AgI 9.450, 14.490. C_8H_8ICl. Calculated (mg): AgCl + AgI 9.680, 14.30.

Iodochlorostilbene. 7.830, 5.870 mg of substance. Found (mg): AgCl + AgI 8.490, 6.260. $C_{14}H_{12}ICl$. Calculated (mg): AgCl + AgI 8.640, 6.460.

SUMMARY

1. The reaction of a number of unsaturated compounds with hydrochloric acid solutions of iodine trichloride was studied. Styrene, stilbene, petroselinic and oleic acids, ethyl petroselinate and ethyl cinnamate form iodochloro derivatives with hydrochloric acid solutions of ICl_3; under the same conditions dial and cinnamic acid form iodohydrins.

2. For purposes of comparison the reaction of the same unsaturated compounds with a hydrochloric acid solution of ICl was studied. It was shown that iodine chloride and iodine trichloride form the same reaction products.

LITERATURE CITED

[1] V. Sorokhin, J. Russ. Chem. Soc. 3, 192 (1871).

[2] S. Tanatar, J. Russ. Chem. Soc. 25, 97 (1893).

[3] E. Erlenmeyer, Lieb. Ann. 289, 259 (1896).

[4] J. A. Wijs, Z. ang. Ch. 11, 291 (1898).

[5] A. Michael, J. pr. Chm. (2), 60, 448 (1899).

[6] H. Jngle, J. Soc. Chem. Ind. 21, 587 (1902); 23, 422 (1904).

[7] A. V. Istomin, J. Russ. Chem. Soc. 36, 1199 (1904).

[8] J. Böeseken, E. Gelber, Rec. trav. chim. 46, 158 (1927); 48, 377 (1929).

[9] A. I. Gengrinovich, V. F. Kramarenko, Sci. Records Kiev. Post-Grad. Inst. of Medicine of Pharmacists, 1, 87 (1950); A. I. Gengrinovich, Milk Ind. 6, 29 (1954).

[10] T. I. Temnikova, Z. A. Basova, M. A. Khaimova, J. Gen. Chem., Symp., II, 874 (1953).

[11] A. I. Nesmeyanov, R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1943, 152.

*Chloroform does not extract ICl and ICl_3 from hydrochloric acid solutions.

[12] E. M. Brainina, R. Kh. Freidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1950, 314.

[13] Ya. A. Fialkov, F. E. Kagan, Ukr. Chem. J. 18, 64 (1952).

[14] Ya. A. Fialkov, L. I. Rapoport, J. Gen. Chem. 25, 2265 (1955).•

Received October 8, 1956

Kiev Post-Graduate Institute of Medicine

• Original Russian pagination. See C. B. Translation.

THE REPLACEMENT OF THE HALOGEN ATOM IN PHENAZINE HALIDES BY METHOXY, HYDROXY, AMINO AND MERCAPTO GROUPS

V. P. Chernetsky

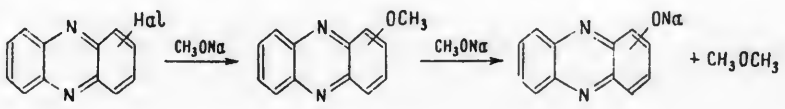
After unsuccessful attempts by Wrede and Mühlroth to replace the chlorine atom in 1-chlorophenazine [1] by other substituents, investigators turned their attention to N-hydroxyphenazine halides where the halogen atom is more mobile [2-4]. Recently, Pachter and Kloetzel obtained 2-ethoxyphenazine by heating 2-chlorophenazine with aqueous-alcoholic alkali and 2-aminophenazine by using an aqueous solution of ammonia [5].

For this purpose we used alcoholic solutions of sodium methylate and ammonia. When 1-chlorophenazine was heated with a solution of sodium methylate at 140°, 1-methoxyphenazine was obtained with a yield of about 80%. A similar reaction with 2-chlorophenazine and 2,3-dichlorophenazine at a lower temperature gave 2-methoxy- and 2,3-dimethoxyphenazines with yields of more than 90%. When 1-methoxy-8-bromophenazine was heated for a short time on a boiling water bath, a small amount of 1,8-dimethoxyphenazine was obtained. In a similar experiment with 1-methoxy-6-bromophenazine, the replacement of the halogen and the formation of 1,6-dimethoxyphenazine were almost complete. It was established, therefore, that the replacement of halogen atoms by a methoxy group in the β-position of the phenazine ring proceeds more rapidly and at a lower temperature than in the α-position.

By heating 1- and 2-chloro- and 2,3-dichlorophenazines with a solution of sodium methylate at 160-200°, we obtained the corresponding hydroxy derivatives; in these reactions it was also noted that a higher temperature is required for the replacement of a halogen atom in the α-position. When 1,2-dichlorophenazine was heated for a short time at 160° a hydroxy derivative, which was evidently 2-hydroxy-1-chlorophenazine, was obtained. These experiments showed that the replacement of the halogen atom in phenazine halides by a hydroxy group could be used as a method for preparing hydroxyphenazines.

Since a small amount of methoxy derivatives, which were probably intermediate products, was obtained in the experiments on the replacement of a halogen atom by a hydroxy group, experiments were carried out on the dealkylation of methoxyphenazines by heating with a solution of sodium methylate in methyl alcohol. Yields of 70-80% of 1- and 2-hydroxyphenazines were obtained from 1- and 2-methoxyphenazines.

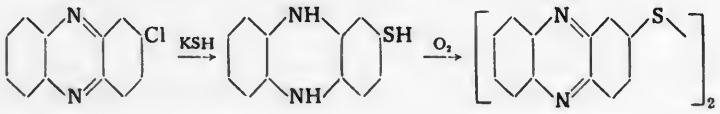
The replacement of a halogen atom by a hydroxy group when heated with sodium methylate may be represented by the following system



1- and 2-Chlorophenazines were used for studying the replacement of a halogen atom by an amino group. When 1-chlorophenazine was heated continuously in a sealed tube with a 25% aqueous solution of ammonia, a yield of more than 30% of 1-aminophenazine was obtained. Heating 2-chlorophenazine with an aqueous-alcoholic solution of ammonia gave a 34% yield of 2-aminophenazine (13% according to Pachter and Kloetzel's data [5]).

2-Chlorophenazine was used for the replacement of a chlorine atom by a mercapto group. When 2-chlorophenazine was treated with an alcoholic solution of potassium hydrosulfide in the cold the only reaction was the

reduction to blue phenazhydrin. If the reaction was carried out with boiling, a bluish-red solution of potassium dihydrophenazinylmercaptide was obtained, from which yellow, 2,2'-diphenazinyldisulfide was precipitated on standing in air. The reaction proceeded in accordance with the following system



The addition of acetic acid precipitated light yellow 2-mercaptodihydrophenazine from the bluish-red solution; this mercapto compound was oxidized in air to green phenazhydrin and then to yellow 2,2'-diphenazinyldisulfide. The use of 10-hydroxy-2-chlorophenazine as the initial substance gave the same results.

EXPERIMENTAL

The replacement of the halogen atom by methoxy and hydroxy groups. The reaction involving the replacement of the halogen atom by methoxy and hydroxy groups was carried out as follows. Methyl alcohol was added to narrow thick-walled test tubes, metallic sodium was introduced and a weighed sample of the phenazine halides was added to the solution. The tubes were carefully sealed and heated on a boiling water bath or in a metal heating unit. When heating was finished, the tubes were opened, the mixture was diluted with water and heated to evaporate the methyl alcohol; the yellow precipitates which had formed were filtered. The alkoxy derivatives were separated chromatographically from the precipitates on aluminum oxide and by crystallization; the hydroxyphenazines were precipitated from the intensely colored mother liquors by acetic acid. The hydroxyphenazines were acetylated by boiling with acetic anhydride and were identified by means of a mixed melt with the known compounds.

A. Replacement by a methoxy group.

1. 0.2 g of 1-chlorophenazine, 0.1 g of metallic sodium and 4 ml of methyl alcohol were heated, as indicated above, at 140° for 3 hours. 0.155 g (79.5%) of 1-methoxyphenazine [6] [yellow needles with an m. p. of 167-168° (from ligroin) (a mixed melt with 1-methoxyphenazine obtained by a different method showed no depression of the melting point)] and 0.035 g (19%) of 1-hydroxyphenazine in the form of a yellow precipitate (from the red-violet filtrate) were obtained.

2. 0.3 g of 2-chlorophenazine was heated with a solution of 0.15 g of sodium in 4.5 ml of methyl alcohol on a boiling water bath for 1.5 hours. 0.28 g (96%) of 2-methoxyphenazine [7] was obtained: it was in the form of yellow needles with an m. p. of 123-124° (from petroleum ether) (a mixed melt with pure 2-methoxyphenazine gave no depression of the melting point).

3. 0.1 g of 2,3-dichlorophenazine was heated with a solution of 0.1 g of sodium in 2 ml of methanol for 5.5 hours at 100-105°. 88 mg (91.5%) of 2,3-dimethoxyphenazine [8] was obtained: it was in the form of pale yellow needles with an m. p. of 229-230° (from benzene).

Found %: N 11.60, 11.53. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.66.

4. 0.3 g of 1-methoxy-8-bromophenazine was heated with a solution of 0.3 g sodium in 6 ml of methyl alcohol for 4 hours on a boiling water bath. 0.22 g of undissolved 1-methoxy-8-bromophenazine was regenerated and 40 mg of 1,8-dimethoxyphenazine [9] was obtained: it was in the form of bright yellow needles with an m. p. of 259-260° (from a mixture of benzene with ligroin); a mixed melt with pure 1,8-dimethoxyphenazine showed no depression of the melting point).

5. 0.1 g of 1-methoxy-6-bromophenazine was heated with a solution of 0.1 g of sodium in 3 ml of methanol for 3.5 hours on a boiling water bath. 78 mg (94%) of 1,6-dimethoxyphenazine [9] was obtained: it was in the form of yellow needles from methyl alcohol; the m. p. was 172-173°. A mixed melt with pure 1,6-dimethoxyphenazine showed no depression of the melting point.

B. Replacement by a hydroxy group.

1. 0.3 g of 1-chlorophenazine was heated with a solution of 1.5 g of sodium in 6 ml of methanol at 160-165° for 2.5 hours. 0.19 g (69.5%) of 1-hydroxyphenazine [10] was obtained: it was in the form of yellow needles with an m. p. of 140-145° (from a mixture of ligroin and benzene). The acetyl derivative was in the form of yellow needles with an m. p. of 121-122° (from alcohol). A mixed melt with pure 1-acetoxyphenazine showed no depression of the melting point. 0.04 g (13.6%) of 1-methoxyphenazine was obtained from the water-insoluble precipitate.

2. 0.2 g of 2-chlorophenazine was heated in a solution of 0.1 g of sodium in 4 ml of methyl alcohol at 150-160° for 4 hours. 0.146 g (80%) of 2-hydroxyphenazine [11] was obtained. The acetyl derivative was in the form of pale yellow needles with an m. p. of 156-158°. A mixed melt with 2-acetoxyphenazine, obtained in a different manner, showed no depression of the melting point. 0.035 g (18%) of yellow 2-methoxyphenazine with an m. p. of 122-123° was obtained from the residue on the filter.

3. 0.3 g of 1,2-dichlorophenazine was heated with a solution of 0.2 g of sodium in 8 ml of methyl alcohol at 150-160° for 4.5 hours. 0.27 g (97%) of the hydroxy derivative was obtained. The acetyl derivative was in the form of light yellow plates with an m. p. of 199-200° (from a mixture of benzene and ligroin).

Found %: N 10.02, 10.30; Cl 12.80. $C_{14}H_2O_2N_2Cl$. Calculated %: N 10.27; Cl 13.02.

4. 0.1 g of 1,8-dichlorophenazine was heated with a solution of 0.1 g of sodium in 3 ml of methyl alcohol at 200° for 8.5 hours. 60 mg (71%) of the yellow dihydroxy derivative was obtained. The diacetyl derivative was in the form of yellow needles with an m. p. of 253-256° [12] (from aqueous alcohol). A mixed melt with 1,8-diacetoxyphenazine showed no depression of the melting point.

5. 0.1 g of 2,3-dichlorophenazine was heated with a solution of 0.1 g of sodium in 2 ml of methyl alcohol for 15 hours at 180-200°. 80 mg (94%) of the bright red dihydroxy derivative with an m. p. of 249-251° was obtained. The diacetyl derivative was in the form of pale yellow needles with an m. p. of 239-240° (from alcohol).

Found %: N 9.47, 9.48. $C_{16}H_{12}O_4N_2$. Calculated %: N 9.46.

A mixed melt with 2,3-diacetoxyphenazine obtained from 2,3-diaminophenazine [13] showed no depression of the melting point.

Replacement of a methoxy group by a hydroxy group.

1. 0.3 g of 1-methoxyphenazine was heated with a solution of 0.15 g of sodium in 6 ml of methyl alcohol at 165° for 4 hours. 0.275 g (98%) of 1-hydroxyphenazine was obtained. The acetyl derivative was in the form of light yellow needles with an m. p. of 120-121° (from aqueous alcohol). A mixed melt with 1-acetoxyphenazine obtained in a different manner showed no depression of the melting point.

2. 0.2 g of 2-methoxyphenazine was heated with a solution of 0.1 g of sodium in 4 ml of methyl alcohol at 160° for 6 hours. 0.15 g (89%) of 2-hydroxyphenazine was obtained; it was in the form of yellow needles with an m. p. of 262-263° (with decomp.) (from benzene and alcohol). The acetyl derivative was in the form of light yellow needles with an m. p. of 157-158°. A mixed melt with 2-acetoxyphenazine obtained in a different manner showed no depression of the melting point. 20 mg of unreacted 2-methoxyphenazine was recovered.

Replacement of a chlorine atom by an amino group.

1. 0.6 g of 1-chlorophenazine was sealed in a tube with 9 ml of a 25% aqueous solution of ammonia and heated in a metal heating unit for 70 hours at 210-230°. The tube was opened and the reaction product was treated with boiling benzene. The red-brown benzene solution was filtered and extracted with 4% hydrochloric acid. The amino derivative was precipitated in the form of a red amorphous substance. 0.15 g (33.5%) of 1-aminophenazine [14] was obtained. After crystallization from a mixture of benzene and ligroin, dark red needles with an m. p. of 179-180° were obtained. A mixed melt with the compound obtained by a different method showed no depression of the melting point.

2. 0.9 g of 2-chlorophenazine was heated with 9 ml of a 25% aqueous solution of ammonia and 6 ml of ethyl alcohol at 220° for 13 hours. After they had cooled the sealed tubes were opened, the solid substance was filtered and extracted with 4% hydrochloric acid in the form of an intense red solution. The hydrochloric acid solution was filtered and the product was precipitated with ammonia. 0.28 g (34%) of 2-aminophenazine [15] was obtained: it was in the form of red needles which melted at 275-277° (followed by decomposition). A

mixed melt with 2-aminophenazine obtained in a different manner showed no depression of the melting point.

Replacement of a chlorine atom by a mercapto group.

1. 1 g of 2-chlorophenazine was dissolved with heating in 20 ml of alcohol. The solution was rapidly cooled and 5 ml of an alcoholic solution of potassium hydrosulfide containing 1.75 g of potassium hydrosulfide was added to the precipitated mixture. The mixture was boiled for 1.5 hours. The bluish-red solution was filtered and left for several days; a yellow precipitate was gradually deposited. 0.55 g of 2,2'-diphenazinyldisulfide was obtained: it was in the form of fine, pale yellow needles with an m. p. of 248-249° (from benzene).

Found %: N 12.97, 13.16; S 15.08, 15.30. $C_{24}H_{14}N_4S_2$. Calculated %: N 13.27; S 15.16.

2. 20 ml of an alcoholic solution of potassium hydrosulfide (containing 6.4 g of potassium hydrosulfide) was added to 5 g of a solution of 10-hydroxy-2-chlorophenazine in 50 ml of alcohol. The mixture turned green in the cold. When the mixture was boiled for 1.5 hours, a bluish-red solution was formed. It was filtered and acidified with acetic acid. A pale yellow precipitate of 2-mercaptodihydrophenazine (4.5 g, quantitative yield) with an m. p. of 195-200° was formed. The dihydro derivative was gradually oxidized in air to green phenazhydrin and then to yellow, 2,2'-diphenazinyldisulfide; a mixed melt of the latter with the compound from the previous experiment showed no depression of the melting point.

SUMMARY

1. The possibility of the replacement of the halogen atom in phenazine halides by methoxy and hydroxy groups when heated with a solution of sodium methylate in methyl alcohol was shown. At temperatures of up to 140° the reaction products are methoxyphenazines, at 160-200° they are hydroxyphenazines, the halogen atom in the β-position being more easily replaceable.

2. By the replacement of the halogen atom in 1-chloro-, 2-chloro-, 2,3-dichloro-, 1-methoxy-6-bromo and 1-methoxy-8-bromophenazines by a methoxy group, the corresponding methoxy- and dimethoxyphenazines were obtained.

3. By the replacement of the halogen atom in 1- and 2-chloro, 1,2-, 1,8- and 2,3-dichlorophenazines by a hydroxy group, the corresponding hydroxy and dihydroxyphenazines were obtained.

4. 30-35% yields of 1- and 2-aminophenazines were obtained by the replacement of the chlorine atom in 1- and 2-chlorophenazines by an amino group.

5. When 2-chlorophenazine and its 10-hydroxy derivative were heated with potassium hydrosulfide in methyl alcohol, 2-mercaptodihydrophenazine was obtained; this rapidly oxidized in air to 2,2'-diphenazinyldisulfide.

LITERATURE CITED

[1] F. Wrede, O. Mühlroth, Ber. 63, 1931 (1930).

[2] D. L. Vivian, J. Am. Chem. Soc. 71, 1139 (1949).

[3] D. L. Vivian, J. Am. Chem. Soc. 73, 457 (1951).

[4] I. Ya. Postovsky, E. I. Abramova, J. Gen. Chem. 24, 485 (1954).*

[5] I. J. Pachter, M. C. Kloetzel, J. Am. Chem. Soc. 74, 971 (1952).

[6] F. Wrede, E. Strack, Ber. 62, 2051 (1929).

[7] H. McCombie, H. A. Scarborough, W. A. Waters, J. Chem. Soc. 1928, 353.

[8] R. Z. Slack, R. Slack, Nature, 160, 437 (1947); D. L. Vivian, J. Org. Ch. 21, 824 (1956).

[9] S. B. Serebryanyi and V. P. Chernetsky, J. Gen. Chem. 21, 2033 (1951).*

[10] F. Wrede, E. Strack, Z. physiol. Ch. 177, 177 (1928).

[11] F. Kehrmann, F. Cherpillod, Helv. Chim. Acta, 7, 973 (1924).

*Original Russian pagination. See C. B. Translation.

[12] S. B. Serebryany, J. Gen. Chem. 22, 702 (1952).*

[13] O. Fischer, E. Hepp, Ber. 23, 841 (1890); T. Ullmann, F. Mautner, Ber. 35, 4302 (1902).

[14] F. Kehrmann, P. Prunier, Helv. Chim. Acta, 7, 984 (1924).

[15] O. Fischer, E. Hepp, Ber. 22, 355 (1889).

Received October 6, 1956

Institute of Organic Chemistry
Academy of Sciences, USSR

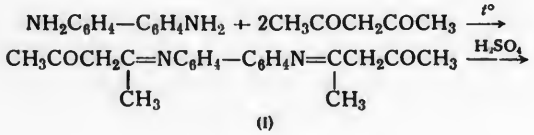
* Original Russian pagination. See C. B. Translation.

THE SYNTHESIS OF SUBSTANTIVE DYES OF THE BIQUINOLINE SERIES

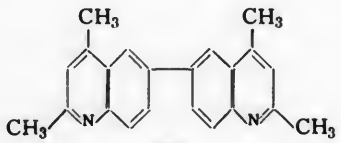
L. N. Goldyrev

Until recently, methylated 6,6'-biquinolines, which are used as initial raw materials in the synthesis of substantive dyes, were only obtained by the Baeyer reaction with a yield of 17 to 51% [1-3]. A. E. Porai-Koshits, who studied the chemistry of these dyes, came to the conclusion that "biquinoline yellow itself could acquire practical importance and become the parent substance of a new class of biquinoline dyes if an inexpensive method could be found for providing good yields of biquinaldine and its derivatives from benzidine and its derivatives [1]."

Meanwhile, it was possible to use the Combes-Turner reaction [4, 5] for obtaining biquinoline derivatives.



(I)



(II)

In contrast to the Baeyer reaction (which is based on the complex condensation of aromatic amines and a mixture of acetaldehyde, acetone, and hydrochloric acid), the Combes-Turner reaction gives very high yields of anils (I) which are easily cyclized to biquinolines (II). When biquinolines are obtained by the Baeyer reaction, a considerable amount of tar is formed, and this has a marked effect on the yield of the desired products. A comparison of the yields of biquinoline derivatives with both reactions is given in Table 1.

TABLE 1

Initial substances	Yield of the derivatives of biquinolines (%)	
	by the Baeyer reaction	by the Combes-Turner reaction
Benzidine	31.0 [1, 2]	90.0
o-Tolidine	51.0 [1, 2]	95.0
4,4'-Diaminodiphenylmethane	Not obtained	93.0
4,4'-Diaminoditolylmethane	Not obtained	90.0

It must be mentioned that the Combes-Turner reaction does not give biquinoline derivatives in all cases. For example, although o-dianisidine gives high yields of an anil, the latter, like the simpler anil from o-anisidine [6], does not cyclize. The causes of these phenomena are explained by us.

The synthesized 2,2',4,4'-tetramethylbiquinoline, 2,2',4,4',8,8'-hexamethylbiquinoline, 2,2',4,4'-tetramethyl-6,6'-biquinolylmethane and 2,2',4,4',8,8'-hexamethyl-6,6'-biquinolylmethane were converted by fusing with phthalic anhydride into the corresponding biquinophthalones and the latter were sulfonated to form dyes. With the initial substances as a basis the dyes may be placed in the following order with respect to their substantive action (on cotton): o-tolidine > benzidine > 4,4'-diaminoditolylmethane > 4,4'-diaminodiphenylmethane.

The opinion of A. E. Porai-Koshits [1] that the introduction of methylene groups which separate the quinoline rings must reduce the color and substantivity was, therefore, confirmed. It is possible that this phenomenon is connected with a disturbance of the coplanarity of the molecules, to which B. M. Krasovitsky [7] devoted his attention.

EXPERIMENTAL

Preparation of the anils (I).* 0.05 mole portions of the following substances were introduced in 0.11 mole of acetylacetone: benzidine, o-tolidine, o-dianisidine, 4,4'-diaminodiphenylmethane and 4,4'-diaminoditolylmethane. The mixture was, in each case, heated on a boiling water bath for 2 hours, during which time the substances dissolved, water was liberated and, in some instances, a precipitate was formed. The substance was washed with dilute acetic acid (1 : 30) to remove the initial substances. The residues obtained after washing were dried at 105°. The solid anils were recrystallized from alcohol until compounds with constant melting points were obtained.

The following yields of anils were obtained: from benzidine, 96%; from o-tolidine, 95%; from o-dianisidine, 68.5%.

The anil from 4,4'-diaminodiphenylmethane was an oil, readily soluble in alcohol, ether and benzene; the yield was 74.4%.

The anil from 4,4'-diaminoditolylmethane was obtained with a yield of 90%; the m. p. was 108°.

Found: M 382.4 (by Rast's method). $C_{25}H_{32}O_2N_2$. Calculated %: M 392.5.

Preparation of the derivatives of biquinoline (II) and dyes. 0.04 Mole of the anil was dissolved in 0.96 mole of concentrated sulfuric acid for 1 hour with heating on a boiling water bath. The solution was then poured into water, made alkaline and the precipitate of the biquinoline derivative which was formed was filtered. After they had been dried, the products were recrystallized from pyridine or alcohol until a constant melting point was obtained.

Biquinoline derivatives were obtained with the following yields: from benzidine, 2,2',4,4'-tetramethylbiquinoline, m. p. 231°, 90%; from o-tolidine, 2,2',4,4',8,8'-hexamethylbiquinoline, m. p. 242°, 95%; from 4,4'-diaminodiphenylmethane, 2,2',4,4'-tetramethyl-6,6'-biquinolylmethane, m. p. 148°, 93%; from 4,4'-diaminoditolylmethane, 2,2',4,4',8,8'-hexamethyl-6,6'-biquinolylmethane, m. p. 142°, 90%.

Determination of the molecular weight (by Rast's method).

2,2',4,4',8,8'-Hexamethylbiquinoline. Found: M 339.7. $C_{24}H_{24}N_2$. Calculated: M 340.4.

2,2',4,4'-Tetramethyl-6,6'-biquinolylmethane. Found: M 334.1. $C_{23}H_{22}N_2$. Calculated: M 326.4.

2,2',4,4',8,8'-Hexamethyl-6,6'-biquinolylmethane. Found: M 360.0. $C_{25}H_{26}N_2$. Calculated: M 354.5.

In contrast to the other anils described above, the anil from o-dianisidine did not cyclize after heating with sulfuric acid but underwent rupture, o-dianisidine being reobtained.

The methylated biquinolines obtained were converted to dyes by the method described by A. E. Porai-Koshits [1]. The results of our experiments confirm the possibility (indicated by A. E. Porai-Koshits [1]), of obtaining biquinophthalones and dyes, in high yields.

The dyes obtained dyed cotton cloth in an acid bath under identical conditions and this made it possible to compare their substantivity. The deepest color was produced by the dye obtained from o-tolidine; the weakest

* Together with the students A. V. Borisova and L. N. Goldshtein.

color was produced by the dye from 4,4'-diaminodiphenylmethane.

We wish to thank V. I. Esarov for his advice.

SUMMARY

1. It was shown that 2,2',4,4'-tetramethylbiquinoline and 2,2',4,4',8,8'-hexamethylbiquinoline are obtained with much higher yields by the Combes-Turner reaction than by the Baeyer reaction.

2. It was shown that the anil from o-dianisidine cannot cyclize in the presence of sulfuric acid.

3. Starting with 4,4'-diaminodiphenyl- and 4,4'-diaminoditolylmethanes the following new methylbiquinolines were synthesized by the Combes-Turner reaction: 2,2',4,4'-tetramethyl6,6'-biquinolylmethane and 2,2',4,4', 8,8'-hexamethyl-6,6'-biquinolylmethane.

4. It was shown that in the case of dyes obtained from biquinoline derivatives containing methylene groups which separate the quinoline rings, the color and the substantivity are reduced.

LITERATURE CITED

[1] A. E. Porai-Koshits and A. I. Kulikov, J. Gen. Chem. 8, 124 (1938).

[2] B. I. Ardashev and Z. V. Malina, J. Gen. Chem. 21, 1349 (1951).*

[3] B. I. Ardashev, Progr. Chem. 23, 45 (1954).

[4] M. Alph, Combes, Bull. Soc. Chim. (2) 49, 89 (1888).

[5] E. E. Turner, J. Chem. Soc. 107, 1495 (1915).

[6] W. Koenigs, A. Mengel, Ber. 37, 1333 (1904); E. Ruberts, E. E. Turner, J. Chem. Soc. 1927, 1832.

[7] B. M. Krasovitsky, Ukr. Chem. J. 21, 71 (1955).

Received October 6, 1956

Urals State University

*Original Russian pagination. See C. B. Translation.

VINYLATION OF D-GLUCOSE AND ITS ACETONE DERIVATIVE. 1.

B. I. Mikhantyev and V. L. Lapenko

Vinylation of alcohols and phenols by the method of A. E. Favorsky and M. F. Shostakovsky [1] has become very widespread. In the last five years the reaction with α-methylglucoside has been studied, and also the reaction of cellulose with acetylene [2, 3].

The present work describes the vinylation of D-glucose and its diacetone derivative. Glucose caramelized and formed tars, and the yield of divinyl-D-glucose did not exceed 6%. A good yield of the monovinyl derivative was obtained for diacetone glucose (55%).

EXPERIMENTAL

Experiment 1. A mixture of 30 g of D-glucose, 270 ml of acetone, and 3 g of KOH was placed in an autoclave under an acetylene pressure of 20 atm. at 18°. When the autoclave was rotated and heated for 4 hours at 140°, the pressure rose to 70 atm. The reaction mixture was red-brown. Caramelized glucose was found at the bottom of the autoclave. Distillation separated a light yellow, oily liquid which boiled at 105-110° (2 mm), decolorized bromine water, n_D^{20} 1.4550. The yield was 2.2 g (5.8%). The product was very impure, but, according to analysis for C and H and the number of hydroxyl groups, it was the divinyl derivative of D-glucose, with the vinyl groups in unknown positions.

Experiment 2. The autoclave was filled with 20 g of 1,2;5,6-diisopropylidene-D-glucose [4], 300 ml of dioxane, and 4 g of KOH. The acetylene pressure at 18° was 25 atm. Vinylation was continued for 7 hours at 150°. The greatest pressure was about 90 atm. The dark red reaction mixture was filtered and then distilled. The oily liquid which resulted decolorized bromine water and was easily soluble in organic solvents. The yield was 12 g (54.5%).

B. p. 115-116° (1.5 mm), d_{20}^{20} 1.171, n_D^{20} 1.468; MR_D 68.09; calc. 69.69.
Found %: C 59.20, 59.10; H 7.30, 7.28. M 281. $C_{14}H_{22}O_6$. Calculated %: C 58.70; H 7.68. M 286.1.

Hydrogenation of 3-vinyl-1,2;5,6-diisopropylidene-D-glucose. Twenty-five g of substance and 3 g of porous nickel were used for the hydrogenation. The reaction lasted 32 hours. About 1900 ml of hydrogen was absorbed. The catalyst was filtered off and the alcohol (100 ml) was distilled. The remaining fraction was a light yellow, oily liquid with b. p. 105-106° (1.5 mm). The yield of 3-ethyl-1,2;5,6-diisopropylidene-D-glucose was 20 g (77%).

B. p. 105-106° (1.5 mm), d_{20}^{20} 1.138, n_D^{20} 1.520, MR_D 68.30; calc. 70.11.
Found %: C 58.80, 58.70; H 8.51, 8.03. M 284. $C_{14}H_{24}O_6$. Calculated %: C 58.30; H 8.33; M 288.1.

Incomplete hydrolysis of 3-vinyl-1,2;5,6-diisopropylidene-D-glucose. A two-necked flask with a reflux condenser and a mechanical stirrer was filled with 25 g of substance and 25 ml of 96% ethyl alcohol. At 18-20°, 20 drops of concentrated sulfuric acid were added. The white, microcrystalline precipitate was dissolved with excess alcohol. The sulfuric acid was neutralized with 25% aqueous ammonia. The ammonium sulfate was filtered off. The filtrate was evaporated in a vacuum. The solid residue was ground and then washed with ether to remove traces of diacetone glucose and its vinyl ether. The substance was then dissolved in anhydrous alcohol and the solution filtered to remove traces of ammonium sulfate. The filtrate was evaporated in a vacuum. The resulting solid melted at 159-60°. The yield was 10 g (62.5%). 5,6-Isopropylidene-D-glucose melts at 161-162.5° [5].

Heating monovinyldiisopropylideneglucose with dilute sulfuric acid on a boiling water bath formed glucose.

SUMMARY

1. 3-Vinyl-1,2;5,6-diisopropylidene-D-glucose was synthesized from diacetone-D-glucose and acetylene.

2. Hydrogenation of 3-vinyl-1,2;5,6-diisopropylidene-D-glucose gave 3-ethyl-1,2;5,6-diisopropylidene D-glucose.

LITERATURE CITED

[1] A. E. Favorsky, M. F. Shostakovsky, J. Gen. Chem. 13, 1 (1943).

[2] V. V. Shtishevsky, A. A. Obolonskaya, N. I. Nikitin, J. Appl. Chem. 24, 1045 (1951).*

[3] M. F. Shostakovsky, E. N. Prilezhaeva, L. V. Tsymbal, Proc. Acad. Sci. USSR 96, 99 (1954); J. Gen. Chem. 26, 3, 739 (1956).*

[4] Irvine, Hynd, J. Chem. Soc. 95, 1223 (1909).

[5] E. Fiscner, Ber. 28, 2496 (1895).

Received September 28, 1956

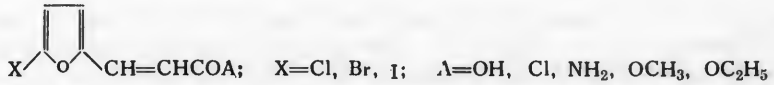
Voronezh State University

* Original Russian pagination. See C. B. Translation.

5-HALOFURYLACRYLIC ACIDS AND THEIR DERIVATIVES

Z. N. Nazarova and M. I. Pimenova

Recently, the search for new methods of using 2-furaldehyde has roused interest in various furan derivatives. Since the 5-halofurylacrylic acids and their derivatives have been little studied, and the physiological activity of some derivatives of furylacrylic acid is interesting [1], we synthesized 5-chloro-, 5-bromo-, and 5-iodofurylacrylic acids by the Perkin reaction and obtained a series of their derivatives.



X=Cl, Br, I; A=OH, Cl, NH_2, OCH_3, OC_2H_5

It is known from the literature that 5-bromofurfural [2] and also 5-iodofurfural [3] easily undergo the Perkin reaction to form the corresponding 5-bromo- and 5-iodofurylacrylic acids. The literature does not describe such a reaction with 5-chlorofurfural. There is only a patent [4] which mentions the possibility of obtaining the methyl ester by condensation of 5-chlorofurfural with methyl acetate in the presence of metal alcoholates.

We have obtained 5-chlorofurylacrylic acid by the Perkin reaction with a yield of 85%; and also its methyl ester.

We have raised the yield of 5-bromofurylacrylic acid from the 56% described in the literature [2] to 87.6% by using potassium acetate instead of sodium acetate and keeping the temperature at 140-142°, at the same time showing that the use of pyridine does not increase the yield of acid. The action of thionyl chloride on bromofurylacrylic acid in benzene solution gave 56% of the acid chloride of 5-bromofurylacrylic acid, identical with the product of bromination of furylacrylic acid chloride [5]. The acid chloride furnished the amide and methyl and ethyl esters of 5-bromofurylacrylic acid, the latter identical with the bromination product of ethyl furylacrylate [6]. The methyl ester was also obtained directly from the acid.

No derivative of 5-iodofurylacrylic acid has been described in the literature. The acid chloride was obtained from the acid and thionyl chloride in benzene solution, but not in pure form, since, when the solvent was distilled, there was decomposition accompanied by separation of iodine. The formation of the acid chloride was established by preparing from it methyl-and ethyl-5-iodofurylacrylate. The methyl ester was also obtained from the acid itself.

An attempt to obtain methyl-5-iodofurylacrylate by an exchange reaction between methyl-5-bromofurylacrylate and KI led only to saponification of the ester with formation of 5-bromofurylacrylic acid. However, when the reaction was run in sunlight in the presence of a trace of anhydrous $CuSO_4$ as a catalyst, iodofurylacrylic acid was formed. This shows the decreased activity of the halogen in 5-bromofurylacrylic acid as compared to 5-bromofurfural and 5-bromofurylnitroethylene [3] and the possibility of its activation by adding copper salts and illuminating it with sunlight.

EXPERIMENTAL

I. 5-Chlorofurylacrylic acid. A mixture of 13 g (0.1 mole) of 5-chlorofurfural [7], 17 g (0.173 mole) of twice fused, anhydrous potassium acetate, and 43 g (0.421 mole) of acetic anhydride was heated under reflux on an oil bath for 4 hours at 135-140°. The reaction mass was repeatedly boiled with water and the combined water

extracts were acidified with hydrochloric acid to give 14.6 g (84.9%) of 5-chlorofurylacrylic acid, m. p. 162° (from alcohol), decomposed at 165°; the acid was easily soluble in benzene, dichloroethane, carbon tetrachloride, and ether, and less soluble in alcohol and hot water.

Found %: Cl 20.28, 20.22. Equiv. 170.0. $C_7H_5O_3Cl$. Calculated %: Cl 20.58. Equiv. 172.57.

Methyl ester. A solution of 5 g of chlorofurylacrylic acid in 70 ml of anhydrous methanol was treated with 0.5 ml of concentrated H_2SO_4 and the mixture allowed to stand at room temperature over night. The ester was precipitated from solution by water and the precipitate was filtered, washed with water and dried in a desiccator. Yield 2.7 g (50%), m. p. 35° (from alcohol).

Found %: Cl 19.02. $C_8H_7O_3Cl$. Calculated %: Cl 19.00.

0.1 g of the methyl-5-chlorofurylacrylate was boiled with 10 ml of 5% aqueous NaOH; acidification with hydrochloric acid gave 5-chlorofurylacrylic acid, m. p. 164° (decomposition); (found: equiv. 171).

II. 5-Bromofurylacrylic acid. Heating a mixture of 17.5 g (0.1 mole) of 5-bromofurfural [3], 24 g (0.25 mole) of twice-fused potassium acetate, and 40 g (0.4 mole) of acetic anhydride at an oil bath temperature of 140-142° for 4 hours gave 19 g (87.6%) of bromofurylacrylic acid. The acid was purified through its sodium salt and consisted of almost white needles melting 177-178°.

Acid chloride. A solution of 5.5 g of 5-bromofurylacrylic acid in 40 ml of benzene was heated on an oil bath at 80-90° for 30 minutes while a solution of 3 g of thionyl chloride in 20 ml of anhydrous benzene was added dropwise. At the end of the addition the thionyl chloride mixture was heated 1.5 hours more, the excess thionyl chloride and benzene were distilled off on the water bath, and the residue was distilled in a vacuum. The fraction which boiled at 180-183° at 10 mm was collected, and crystallized completely. M. p. 54-55°. Yield 2.6 g (44%).

Boiling the acid chloride with a 5% solution of NaOH and then acidifying gave the starting bromofurylacrylic acid, m. p. 177-178°.

Amide. A stream of dry ammonia was passed through a solution of 1.995 g of acid chloride in 40 ml of anhydrous benzene. The precipitate which formed was filtered, washed with water, and dried, m. p. 141-142°, yield 1.76 g (95%). Recrystallization from alcohol (using charcoal and precipitating with hot water) raised the melting point without the least decomposition to 148°.

Found %: Br 36.96, 36.71; N 6.47. $C_7H_6O_2NBr$. Calculated %: Br 36.94; N 6.48.

Alkaline hydrolysis of the amide gave 5-bromofurylacrylic acid, m. p. 178-179° (found: equiv. 218.0).

Ethyl ester. A solution of the acid chloride in benzene, prepared from 2.7 g of 5-bromofurylacrylic acid, was treated with excess anhydrous alcohol (30 ml), and the mixture allowed to stand overnight, after which the excess alcohol was removed on the water bath, the residue diluted with water and extracted with ether; the ether extracts were washed with a dilute solution of NaOH and then with water. When the ether was evaporated, the residue crystallized. Yield 1.2 g (39.3%, calculated on the acid), m. p. 41-42° (from petroleum ether).

0.3 g of the ester was boiled with 30 ml of 10% NaOH; acidification with hydrochloric acid gave 5-bromofurfurylacrylic acid (m. p. 175°) (found: equiv. 216.9).

Methyl ester. a) 4 g (0.018 mole) of 5-bromofurylacrylic acid was dissolved in 60 ml of anhydrous methanol, a drop of concentrated H_2SO_4 was added, and the mixture was allowed to stand at room temperature over night. The ester was precipitated by water, filtered, washed with dilute alkali and water and dried in air. Yield 3.45 g (81%); glittering plates, m. p. 62° (from methanol). Found %: Br 34.14. $C_8H_7O_3Br$. Calculated %: Br 34.58.

0.2 g of the ester was boiled with 30 ml of 10% NaOH to give 5-bromofurylacrylic acid, m. p. 175°.

b) The benzene solution of the acid chloride obtained from 2.7 g of 5-bromofurylacrylic acid and 30 ml of methanol gave 1.56 g of the methyl ester (53.4% based on the acid), m. p. 62° (from methanol).

III. 5-Iodofurylacrylic acid. This was obtained according to [3].

Ethyl ester. To a benzene solution of the acid chloride obtained from 2.5 g of 5-iodofurylacrylic acid, 3 g of thionyl chloride, and 30 ml of anhydrous benzene was added 20 ml of anhydrous alcohol and the solution was allowed to stand overnight. It gave 1.2 g of ester (43.5%, based on the acid). M. p. 61-62° (from alcohol).

Found %: I 43.11, 43.27. $C_9H_9O_3I$. Calculated %: I 43.45.

0.1 g of the ester was boiled with 20 ml of 10% NaOH. The acid resulting from the hydrolysis melted at 169-170°.

Found %: I 47.85. Equiv. 262. $C_7H_5O_3I$. Calculated %: I 48.07. Equiv. 264.03.

Methyl ester. a) A mixture of 2.5 g of iodofurylacrylic acid, 3 g of thionyl chloride, 30 ml of anhydrous benzene and 20 ml of methanol gave 1.2 g of the methyl ester (45.6%). M. p. 81-82° (from methanol).

b) A mixture of 1 g of 5-iodofurylacrylic acid, 15 ml of anhydrous methanol, and a drop of concentrated H_2SO_4 gave 0.66 g of the methyl ester (62.8%). M. p. 82° (from methanol).

Found %: I 45.41. $C_8H_7O_3I$. Calculated %: I 45.28.

Boiling 0.1 g of the ester with 20 ml of 10% NaOH gave 0.05 g of acid with m. p. 169-170°. (Found %: I 47.80. Equiv. 263.0).

c) A mixture of 0.5 g of methyl 5-bromofurylacrylate, 1.5 g of anhydrous KI, 25 ml of glacial CH_3COOH and 0.01 g of anhydrous $CuSO_4$ was heated in sunlight for 1/2 hour, after which it was filtered hot and the filtrate poured into ice water, acidified with hydrochloric acid, the precipitate filtered, washed with cold water, and dried in a desiccator over H_2SO_4. The product was 5-iodofurylacrylic acid, m. p. 168° (Found %: I 47.76. Equiv, 262).

SUMMARY

1. The Perkin reaction with 5-chlorofurfural gave 85% of the previously undescribed 5-chlorofurylacrylic acid and its methyl ester.

2. The amide and methyl ester of 5-bromofurylacrylic acid, and the methyl and ethyl esters of 5-iodofurylacrylic acid were obtained for the first time.

3. It was shown that the carboxyl group, free or esterified, decreased the activity of halogen (bromine) in the nucleus; the activity could be increased by adding a catalyst (a copper salt) and illuminating with sunlight.

LITERATURE CITED

[1] H. Gilman, L. C. Heckert, A. P. Hewlett, J. B. Dickey, Zbl. 1933, II, 3126; H. Gilman, R. E. Brown, G. F. Wright, A. P. Hewlett, Zbl. 1931, II, 2324; N. N. Melnikov, Yu. A. Baskakov and K. S. Bokarev, The Chemistry of Herbicides and Plant Growth Hormones.* Goskhimizdat, Moscow, 329 (1954); S. A. Giller, Furacylene and Experiments on its Use,* Izd. AN Latvian SSR, 15 (1953); Am. patent 2 564 663 (1952), News of Chem. Lit. No. 3, 6 (1952).

[2] H. Gilman, G. F. Wright, Rec. trav. chim. 49, 195 (1930).

[3] Z. N. Nazarova, J. Gen. Chem. 25, 539 (1955); 24, 575 (1954).**

[4] English patent 569529 (1945); Ch. A. 42, 928 (1948).

[5] H. Gilman, A. P. Hewlett, G. F. Wright, J. Am. Chem. Soc. 53, 4192 (1931).

[6] A. P. Dunlop, F. N. Peters, The Furans. N. V. 140 (1953); H. Gilman, G. F. Wright, J. Am. Chem. Soc. 52, 3349 (1930); O. Dann, Chem. Ber. 80, 435 (1947).

[7] W. J. Chute, G. F. Wright, J. org. Ch. 10, 541 (1945).

Received August 29, 1956

Rostov-on-Don State University

*In Russian.
**Original Russian pagination. See C. B. Translation.

SYNTHESES AND TRANSFORMATIONS IN THE DIARYLUREA SERIES

II. SYNTHESIS OF CHLORINE-SUBSTITUTED DIARYLUREAS

D. F. Kutepov and N. S. Rozanova

Chlorine-substituted diarylureas are interesting from both theoretical and practical viewpoints. It is known from the literature that 2,2',4,4',6,6'-hexachlorodiphenylurea was obtained by successive chlorinations of diphenylurea on the nitrogen, followed by heating the chlorinated diphenylurea in glacial acetic acid. The chlorine migrated from the nitrogen into the ring, at first forming a dichlorodiphenylurea which was again chlorinated on the nitrogen, etc. This method was very tedious and naturally could not be used practically. In addition, it was hard to get a product by this method in which the degree of chlorination in both rings was the same. When diphenylurea was chlorinated either in organic or aqueous medium, dichloro- and tetrachloro-diphenylureas were obtained along with the hexachlorodiphenylurea; these were very difficult to separate from the hexachloro-compound.

We used the corresponding chloro-substituted anilines to get chemically pure preparations of diphenylurea with chlorine substitution in the rings, since the method of obtaining the anilines was described in the literature [2]. By changing the method slightly we could introduce chlorine into the ring in the positions which we wished for the chlorine-substituted anilines, and by treating them with phosgene we could obtain the chlorine-substituted diarylureas.

We obtained chemically pure preparations of dichloro-, tetrachloro-, and hexachlorodiphenylurea and studied their chemical properties. We thus obtained the three isomeric hexachlorodiphenylureas (the 3,3',4,4',5,5'- and 2,2',4,4',5,5'-hexachlorodiphenylureas had not been previously described).

To obtain them pure, free from any 2,2',4,4',6,6'-hexachlorodiphenylurea, we used a seven-step method of synthesis: we prepared 2,6-dichloro-4-nitroaniline by chlorination of p-nitroaniline; transformed it to 3,5-dichloronitrobenzene and reduced the latter to dichloroaniline; prepared 1,3,5-trichlorobenzene and nitrated it; reduced the trichloronitrobenzene to the corresponding trichloroaniline, and finally treated it with phosgene to get hexachlorodiphenylurea. 3,5-Dichloronitrobenzene was obtained by diazotizing trichloroaniline and treating the diazonium salt with alcohol [3]. The transformation of 3,5-dichloroaniline into 1,3,5-trichlorobenzene was carried out by replacing the amino group in dichloroaniline by chlorine, using the Sandmeyer method [4].

In the synthesis of 3,3',4,4',5,5'-hexachlorodiphenylurea we started from 2,6-dichloro-p-nitroaniline, first replacing the amino group by chlorine by diazotization to give 3,4,5-trichloro-1-nitrobenzene, and reducing the latter with iron filings to the corresponding trichloroaniline. We treated the 3,4,5-trichloroaniline with phosgene to get 3,3',4,4',5,5'-hexachlorodiphenylurea. An analogous method was used to obtain 2,2',4,4',5,5'-hexachlorodiphenylurea.

EXPERIMENTAL

2,2'-Dichlorodiphenylurea. 2,2'-Dichlorodiphenylurea was prepared by treating o-chloroaniline with phosgene in aqueous alkali. A 500 ml four-necked flask was used, fitted with a stirrer, thermometer, reflux condenser, and two tubes, for adding phosgene and for removing the gases formed in the reaction. A mixture of 26 g of o-chloroaniline and 250 ml of water was added to the reaction flask. Over a period of 50 minutes 12.8 g of phosgene was added at 30° with energetic stirring. The reaction mixture was kept alkaline during the whole process by adding calcined soda. The white crystalline precipitate was filtered, washed first with weak hydrochloric acid, then with water, and dried. Thus we obtained 24.8 g (87.6%) of 2,2'-dichlorodiphenylurea, m. p. 235-236°.

Found %: C 55.76, 56.00, H 2.89, 2.91; N 9.56, 9.42. $C_{13}H_{10}ON_2Cl_2$. Calculated %: C 55.51; H 3.59; N 9.92.

3,3'-Dichlorodiphenylurea. m-Chloroaniline and phosgene in an aqueous alkali solution under the conditions described before yield this compound. From 20.2 g of m-chloroaniline we obtained 18.7 g (85.3%, based on the starting aniline) of 3,3'-dichlorodiphenylurea, m. p. 244°.

4,4'-Dichlorodiphenylurea was obtained by treating p-chloroaniline with phosgene. From 26.1 g p-chloroaniline we obtained 26.2 g (92.5% based on p-chloroaniline) of 4,4'-dichlorodiphenylurea, m. p. 270-271°.

2,2',4,4'-Tetrachlorodiphenylurea was obtained by reaction of 2,4-dichloroaniline with phosgene in nitrobenzene. We added 20 g of 2,4-dichloroaniline and 250 ml of nitrobenzene to the reaction flask. After carefully mixing and heating the mixture to 100° we passed in 10 g (an excess) of phosgene over a period of 45 minutes. At the end of passing the phosgene the reaction mass was stirred for another hour, producing a precipitate. The reaction mass was then cooled to 20° and the precipitate was filtered and freed from residual nitrobenzene by steam distillation. The resulting 2,2',4,4'-tetrachlorodiphenylurea was washed with hot water and then hot alcohol. We obtained 19.5 g (90.37%) of product as a white, crystalline powder, m. p. 272-273°; the literature gives 273°.

Found %: N 8.1, 8.04; Cl 39.96, 40.12. $C_{13}H_8ON_2Cl_4$. Calculated %: N 8.00; Cl 40.54.

2,2',4,4',6,6'-Hexachlorodiphenylurea was obtained from 2,4,6-trichloroaniline and phosgene. Over a period of 1 hour a solution of 10 g of 2,4,6-trichloroaniline in 40 ml of nitrobenzene at 130° was treated with a stream of phosgene (3 g). Then the mixture was stirred for 2 hours more at 130° and then gradually cooled. The precipitated hexachlorodiphenylurea was filtered from the nitrobenzene, mixed with 160 ml more of nitrobenzene, and again filtered and then washed on the filter with 80 ml of benzene. The paste of hexachlorodiphenylurea was stirred with 160 ml of water and freed from residual nitrobenzene by steam distillation. We obtained 9.2 g (86.3%) of 2,2',4,4',6,6'-hexachlorodiphenylurea, m. p. 326-327°.

Found %: N 7.14, 6.96. $C_{13}H_6ON_2Cl_6$. Calculated %: N 6.69.

3,3',4,4',5,5'-Hexachlorodiphenylurea was obtained from phsogene and 3,4,5-trichloroaniline. A mixture of 23 g of 3,4,5-trichloroaniline and 250 ml of nitrobenzene was placed in the reaction flask. After careful mixing and heating to 125-130°, 10 g (an excess) of phosgene was passed in at a rate of 0.27 g/min. At the end of the reaction the mass was stirred for another 1.2 hours, producing a precipitate, and then was cooled to 20°. The precipitate was filtered and washed with hot alcohol and the residual nitrobenzene was steam distilled. We obtained 20.3 g (82.8%) of 3,3',4,4',5,5'-hexachlorodiphenylurea as a white powder, insoluble in organic solvents, m. p. 342°. This compound has not been described in the literature.

Found %: N 6.87, 6.77. $C_{13}H_6ON_2Cl_6$. Calculated %: N 6.68.

2,2',4,4',5,5'-Hexachlorodiphenylurea was obtained from phosgene and 2,4,5-trichloroaniline. To obtain the latter we started from 1,2,4-trichlorobenzene which was nitrated with nitric acid. The resulting trichlorobenzene was reduced to 2,4,5-trichloroaniline with iron filings. After careful purification and repeated recrystallizations from alcohol, 2,4,5-trichloroaniline melted at 96-96.5° (the literature reports 96.5°).

Treatment of 2,4,5-trichloroaniline with phosgene in nitrobenzene. In a reaction vessel fitted with a mechanical stirrer, stopcock, outlet tube and inlet bubbler was placed 131 g of 2,4,5-trichloroaniline in 1051 ml of redistilled nitrobenzene. The reaction mixture was heated on an oil bath at 130° and then 36.3 g of phosgene was passed in over 2 hours. The reaction mixture was stirred at 130° for another hour. Then the mixture was cooled and the precipitated hexachlorodiphenylurea was filtered and freed from nitrobenzene by the method described above. The white, crystalline powder melted at 303°. The yield of 2,2',4,4',5,5'-hexachlorodiphenylurea was 90%.

Found %: N 6.96, 7.20; Cl 49.88, 49.48. $C_{13}H_6ON_2Cl_6$. Calculated %: N 6.68; Cl 50.83.

Treatment of 2,4,5-trichloroaniline with phosgene in a water-dichloroethane medium. A solution of 30 g of 2,4,5-trichloroaniline (in 140 ml of dichloroethane), an aqueous solution of soda (26.7 g of Na_2CO_3 in 140 ml of water) and several drops of the emulsifier OP-7 were placed in the reaction flask. With energetic stirring, 15.2 g of phosgene was added through the bubbler. The process lasted 4 hours at a temperature which did not

exceed 20°. The reaction mixture was allowed to stand overnight. The precipitated hexachlorodiphenylurea was filtered, washed on the filter with dichloroethane and hot water, and air dried. We obtained 29.2 g (92%) of 2,2',4,4',6,6'-hexachlorodiphenylurea, m. p. 302-303°. This compound is not described in the literature.

Found %: N 7.53, 7.49. $C_{13}H_6ON_2Cl_6$. Calculated %: N 6.68.

SUMMARY

1. The three isomeric hexachlorodiphenylureas were synthesized; the 2,2',4,4',5,5'- and 3,3',4,4',5,5'-hexachlorodiphenylureas were obtained for the first time.

2. We showed that by treatment with phosgene the corresponding chloroanilines give chlorine-substituted diarylureas in high yield and with a high degree of purity.

LITERATURE CITED

[1] F. D. Chattahay, K. J. P. Orton, Ber. 34, 1078 (1901).

[2] M. K. Bezzubets, V. S. Rozina, J. Appl. Chem. 21, 1152 (1948).

[3] D. Ridg, J. Chem. Soc. 1947, 735.

[4] A. F. Holleman, Rec. trav. Chim. 35, 195 (1917).

Received August 13, 1956

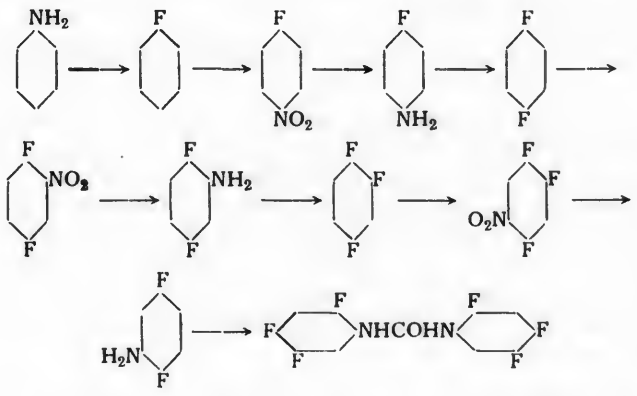
SYNTHESES AND TRANSFORMATIONS IN THE DIARYLUREA SERIES

III. SYNTHESIS OF FLUORINE-SUBSTITUTED DIARYLUREAS

D. F. Kutepov and N. S. Rozanova

Fluorine-substituted diarylureas have not been described in the literature. The synthesis of these compounds is very interesting because of the peculiarities of fluorine itself. It is known from the literature [1] that the distinguishing feature of fluorine among the other elements, especially the halogens, is that the bond of fluorine with carbon is the strongest of all ordinary bonds with that element. On the other hand, fluorine is the most electronegative element; the covalent radius of fluorine differs slightly from the radii of the other halogens. Substitution of fluorine in the aromatic nucleus is very difficult, since the direct action of elementary fluorine on aromatic compounds causes considerable decomposition because of the strong oxidizing action of fluorine. It is true that the literature describes a series of compounds from direct fluorination of organic substances [2], but the data show that in most cases the result of such fluorinations gives only mixtures and not individual compounds in yields which are useful practically. The best method for getting aromatic compounds which contain fluorine in the ring has been, until now, the boron fluoride method developed by Schiemannn [3].

In our work we have synthesized the new 2,2',4,4'-tetrafluoro and 2,2',4,4',5,5'-hexafluorodiphenylureas. The syntheses of these compounds consist of ten steps.



Fluorobenzene was obtained from aniline by the method of Schiemann. This method was also used to introduce the other fluorine atoms into the ring. Nitration of the fluorine derivatives of benzene was carried out either with fuming nitric acid [4] or with a nitrating mixture [5]. Reduction of the nitrocompounds to the corresponding anilines was carried out with iron filings in the presence of acetic acid and the emulsifier OP-7 [6]. The transformation of 2,4,5-trifluoroaniline into 2,2',4,4',5,5'-hexafluorodiphenylurea was performed by treating it with phosphogene in carbon tetrachloride in the presence of the emulsifier OP-7. In the absence of this emulsifier the reaction at 20° proceeds with great difficulty.

2,2',4,4'-Tetrafluorodiphenylurea was synthesized in an analogous way. The starting substance for this synthesis was m-phenylenediamine which was converted into m-difluorobenzene. In this case the Schiemann method was used for simultaneous replacement of the two amino groups by two fluorine atoms. Nitration of

m-difluorobenzene gave 2,4-difluoronitrobenzene which was reduced to 2,4-difluoroaniline. 2,2',4,4'-Tetrafluorodiphenylurea was obtained from 2,4-difluoroaniline and phosgene in carbon tetrachloride in the presence of calcined soda and the emulsifier OP-7.

EXPERIMENTAL

1. Synthesis of 2,2',4,4',5,5'-hexafluorodiphenylurea. Fluorobenzene was obtained from aniline by the Schiemann method [3]. The fluoroboric acid used was prepared by the method described. p-Difluorobenzene, 2,5-difluoronitrobenzene, 1,2,4-trifluorobenzene and 2,4,5-trifluorobenzene were prepared as described in the literature [3, 5, 7].

Preparation of p-fluoronitrobenzene. Fluorobenzene was added dropwise to fuming nitric acid (d 1.5) with stirring at 0-5°. The reaction mixture was poured into ice water which precipitated a heavy oil, easily solidifying; this was p-fluoronitrobenzene with a slight admixture of o-fluoronitrobenzene which was removed by repeated solidification and pressing-out. The yield of p-fluoronitrobenzene was 52%. M. p. 21-22°.

Preparation of p-fluoroaniline. In an iron reactor fitted with stirrer, reflux condenser, thermometer and dropping funnel were placed 696 g of iron filings, 1992 ml of water, 62.5 ml of 40% acetic acid and 2-3 drops of emulsifier OP-7. The mixture was heated to 96-98° and 240 g of p-fluoronitrobenzene was gradually added. At the end of the addition the fluoronitrobenzene mixture was stirred 3 hours more at the same temperature (total reaction time 6.5-7 hours). The p-fluoroaniline was distilled with steam; the distillate was extracted with ether. The ether extract was dried over calcium chloride and redistilled. We obtained 155 g (85.3%) of p-fluoroaniline.

2,5-Difluoronitrobenzene and 2,4,5-trifluoronitrobenzene were obtained in similar ways. The yield of 2,5-difluoroaniline was 73%, and of 2,4,5-trifluoroaniline, 89.2%.

Excess phosgene was passed for 3.5-4 hours at 20° with stirring into a mixture of 98 g of carbon tetrachloride, 28.78 g of calcined soda, 24.8 g of 2,4,5-trifluoroaniline and several drops of emulsifier OP-7. The mixture was allowed to stand overnight. The next day the precipitate was filtered and washed with carbon tetrachloride and water. The yield of 2,2',4,4',5,5'-hexafluorodiphenylurea was 97% based on the starting trifluoroaniline.

The product was a fine white powder, m. p. 234-235°. It was soluble in alcohol, dichloroethane, benzene, and chloroform, insoluble in carbon tetrachloride.

Found %: C 48.75, 49.09. H 1.89, 1.87; N 8.05, 7.84. $C_{13}H_6ON_2F_6$. Calculated %: C 48.71; H 1.87; N 8.74.

2. Synthesis of 2,2',4,4'-tetrafluorodiphenylurea. Preparation of m-difluorobenzene. In the reactor was placed 860 ml of hydrochloric acid (d 1.18). The acid was cooled to 0-10° and 89 g of finely ground m-phenylenediamine was added. The solution of 89 g of phenylenediamine in 860 ml of concentrated hydrochloric acid (d 1.18) was cooled to 0° and 713 ml of a 45% solution of fluoroboric acid was added, and then [8] 190 g of ice, after which a cooled solution of 126 g of sodium nitrite in 156 ml of water was quickly poured in. When the sodium nitrite solution was added, several pieces of solid carbon dioxide were put in the reactor. The salt which precipitated was filtered, washed with cold methanol and ether, and air dried. Decomposition of the fluoroborate was carried out in 20 g portions. The difluorobenzene which was driven off was redistilled twice. We obtained 69 g (73.4%) of m-difluorobenzene.

Preparation of 2,4-difluoronitrobenzene. At −4 to 0°, 20 g of m-difluorobenzene was added dropwise to 90 g of concentrated nitric acid (d 1.5). The mixture was stirred at 0° for another hour, then poured onto ice and extracted with ether. The cold ether extract was washed with a cold, 2% solution of sodium bicarbonate, and then with water. The ether solution of 2,4-difluoronitrobenzene was dried over calcium chloride and distilled. The yield of difluoronitrobenzene was 92.4%.

Preparation of 2,4-difluoroaniline was carried out by reducing the 2,4-difluoronitrobenzene with iron filings in the presence of acetic acid and emulsifier OP-7 by the method described previously. Yield 78%.

A mixture of 2 g of 2,4-difluoroaniline, 2.6 g of calcined soda, 50 ml of carbon tetrachloride, and 2 drops of emulsifier OP-7 was treated over 3 hours with an excess of phosgene, and the mixture was allowed to stand overnight. The next day the precipitate was filtered and washed with water. We obtained 1.9 g of tetrafluorodiphenylurea. When the melting point of the product recrystallized from chloroform was tested, it began to

sublime at 223° and at 260° had fully disappeared without melting. The same effect was observed in a sealed capillary tube. The 2,2',4,4'-tetrafluorodiphenylurea consisted of smooth white needles, very poorly soluble in chloroform and dichloroethane, and almost insoluble in carbon tetrachloride.

Found %: C 54.52, 54.84; H 2.63, 2.76; N 9.98, 9.92. $C_{13}H_8N_2OF_4$. Calculated %: C 54.93; H 2.84; N 9.86.

SUMMARY

1. 2,2',4,4'-Tetrafluorodiphenylurea and 2,2',4,4',5,5'-hexafluorodiphenylurea were synthesized. Neither compound had been described in the literature.

2. It was shown that when fluoroanilines were treated with phosgene a high yield of the corresponding fluorine substituted diarylurea was obtained.

LITERATURE CITED

[1] A. Ya. Yakubovich, Prog. Chem. 25, 3 (1956).

[2] H. Moissan. Le fluor et ses composes. 241 (1900); O. Dimroth, W. Bockemüller, Ber. 64, 516 (1931); W. Bockemüller, Ber. 64, 522 (1931); Lieb. Ann. 506, 20 (1933).

[3] G. Schiemann, R. Pillarsky, Ber. 62, 3039 (1929); J. pr. Ch. 140, 97 (1934).

[4] O. Wallach, Lieb. Ann. 235, 265 (1886).

[5] F. Weygand, R. Löwenfeld, E. F. Möller, Ber. 84, 107 (1951).

[6] M. K. Bezzubets, V. S. Rozina, J. Appl. Chem. 21, 1152 (1948); A. A. Potashnik, V. V. Razumovsky, Auth. Cert. No. 1421.

[7] G. C. Finger, J. Am. Chem. Soc. 73, 145 (1951).

[8] Organic Synth., II, 295 (1943).

Received August 13, 1956

INVESTIGATION OF CARBONYL DERIVATIVES OF BENZENE USING SPECTROGRAPHIC AND OTHER PHYSICOCHEMICAL METHODS

III. INVESTIGATION OF 1,3-DIHYDROXY-4,6-DIACETYLBENZENE AND ITS MONO- AND DIMETHYL ETHERS

F. F. Cheshko and B. G. Distanov

Spectrographic Investigation

1,3-Dihydroxy-4,6-diacetylbenzene. Synthesis was carried out according to the method described by Bakker and Chattaway [1, 2]. The substance was first investigated using the technique reported by Morton and Stubbs [3]. Spectrographic investigation was carried out in isooctane, ethanol, ethanolic solutions of sodium ethoxide, and ethanolic solutions of sulfuric acid at concentrations of 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M.

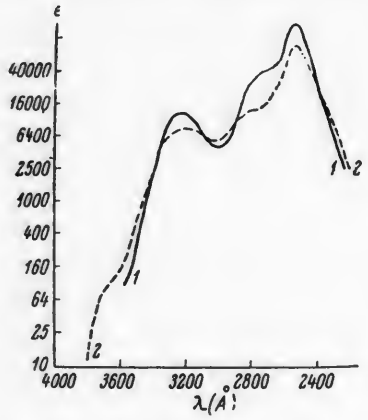


Fig. 1. Ultraviolet absorption spectra. 1) 1,3-Dihydroxy-4,6-diacetylbenzene in isooctane 10^{-2} to 10^{-5} M; 2) the same in ethanol.

The absorption spectrum in isooctane (Fig. 1, curve 1) has absorption bands at λ 3240 A (ε 12,600), λ 2800-2600 A (ε 50,000-27,000)and λ 2520 A (ε 151,400).

The absorption spectrum in ethanol (Fig. 1, curve 2) is the same as that in isooctane, with certain changes. The band in the region λ 2850-2700 A (ε 19,950-11,220) has only one-third the intensity of the isooctane band and is displaced into the long wavelength region by 100 A; the band in the far ultraviolet region has only 1/1.9 the intensity and is not displaced.

The addition of 0.1 of a molecular proportion of sodium ethoxide (per molecular portion of 1,3-dihydroxy-4,6-diacetylbenzene) to the ethanolic solution (Fig. 2, curve 2) causes broadening of the absorption band at λ 3180 A toward the long wavelengths by 200 A. An increase in the ethoxide concentration causes a further displacement of the long-wave edge of the band which reaches 450 A when the concentration reaches 100 molecular proportions of sodium ethoxide per molecular proportion of 1,3-dihydroxy-4,6-diacetylbenzene (Fig. 2, curve 7). The absorption band in the region λ 3700-3550 A (ε 250-287) considerably increases the intensity and acquires a well-defined maximum at λ 3500 A (ε 1600). The absorption band in the central part of the ultraviolet region increases in intensity and simultaneously degenerates when the amount of sodium ethoxide is increased. (Fig. 2, curves 2-6).

The absorption spectrum in ethanolic solution in the presence of 1000 molecular proportions of sulfuric acid (Fig. 3, curve 2) is the same as that in ethanol alone. Increasing the amount of sulfuric acid to 10,000 molecular proportions (Fig. 3, curve 3) causes a displacement of the long-wave part of the absorption spectrum on the average by 200 A toward longer wavelength. When the solution is diluted, the spectrum returns to the absorption spectrum obtained in the presence of 1000 molecular proportions of sulfuric acid. Further increase in the amount of sulfuric acid to 17,000 molecular proportions (Fig. 3, curve 4) causes only a slight displacement

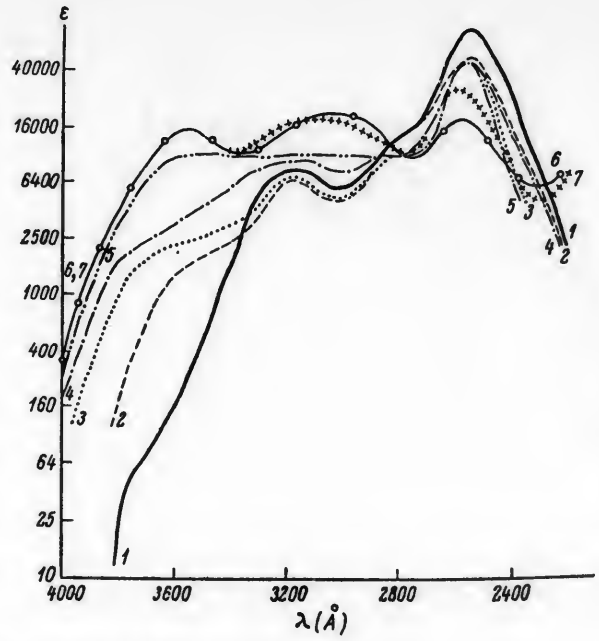


Fig. 2. Ultraviolet absorption spectra.
1) 1,3-Dihydroxy-4,6-diacetylbenzene in ethanol 10^{-2}-10^{-5} M; 2) the same + 0.1 mole C_2H_5ONa; 3) the same + 0.5 mole C_2H_5ONa; 4) the same + 1.0 mole C_2H_5ONa; 5) the same + 2.0 moles C_2H_5ONa; 6) the same + 10 moles C_2H_5ONa; 7) the same + 100 moles C_2H_5ONa.

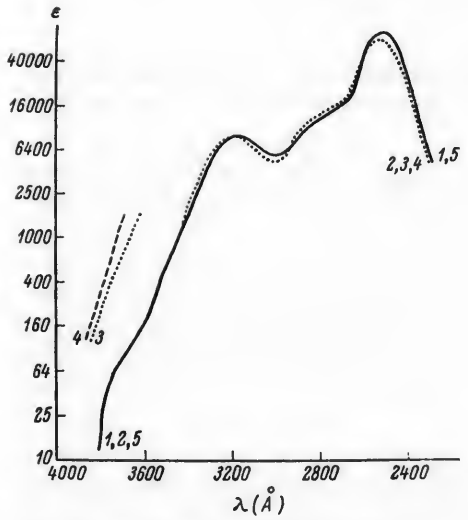


Fig. 3. Ultraviolet absorption spectra.
1) 1,3-Dihydroxy-4,6-diacetylbenzene in ethanol 10^{-2}-10^{-3} M; 2) the same + 1000 molecular proportions of H_2SO_4; 3) the same + 10,000 molecular proportions of H_2SO_4; 4) the same + 17,000 molecular proportions of H_2SO_4; 5) the same + 17,000 molecular proportions of H_2SO_4, after neutralization.

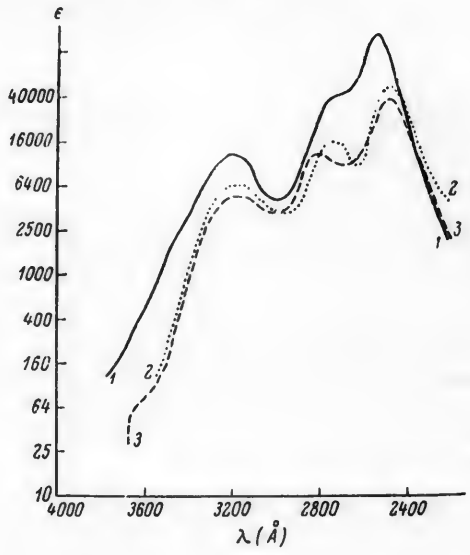


Fig. 4. Ultraviolet absorption spectra.
1) 1,3-Dihydroxy-4,6-diacetylbenzene in isooctane 10^{-2}-10^{-5} M; 2) 1-methoxy-3-hydroxy-4,6-diacetylbenzene in isooctane 10^{-3}-10^{-5} M; 3) the same in ethanol.

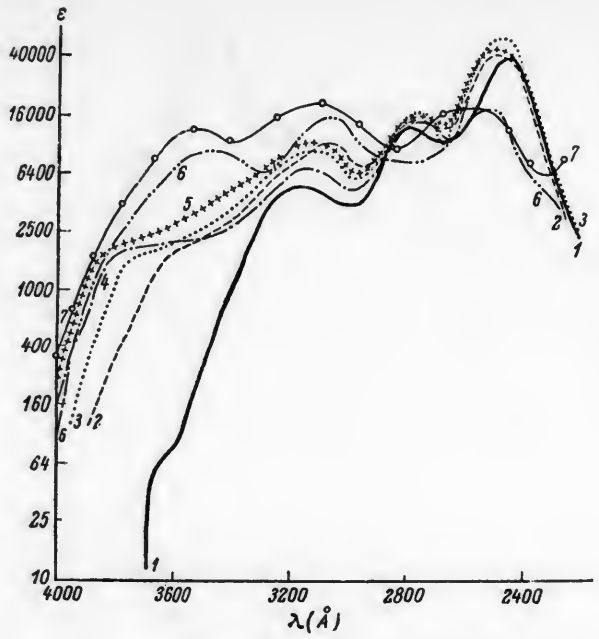


Fig. 5. Ultraviolet absorption spectra.
1) 1-Methoxy-3-hydroxy-4,6-diacetylbenzene in ethanol 10^{-2}-10^{-5} M; 2) the same + 0.1 molecular proportion of C_2H_5ONa; 3) the same + 0.5 molecular proportion of C_2H_5ONa; 4) the same + 1.0 molecular proportion of C_2H_5ONa; 5) the same + 2.0 molecular proportions of C_2H_5ONa; 6) the same + 10 molecular proportions of C_2H_5ONa; 7) the same + 100 molecular proportions of C_2H_5ONa.

of the absorption spectrum toward the long-wave region. The absorption spectrum after neutralization of 17,000 molecular proportions of sulfuric acid corresponds to the absorption of 1,3-dihydroxy-4,6-diacetylbenzene in ethanol (Fig. 3, curve 1).

Monomethyl ether of 1,3-dihydroxy-4,6-diacetylbenzene. The synthesis was based on Mouthner's method [4]. It was carried out without the use of solvent. The monomethyl ether has not been investigated previously. We examined it under the same conditions as 1,3-dihydroxy-4,6-diacetylbenzene.

The absorption spectrum in isooctane and ethanol (Fig. 4, curves 2, 3) has bands at λ 2725 A (ε 16,600), and at λ 2460 A (ε 49,980). Addition of 0.1 of a molecular proportion of sodium ethoxide (Fig. 5, curve 2) causes broadening of the absorption spectrum by 350 A in the direction of the long waves. The absorption intensity increases. Gradual increase in the concentration of the ethoxide to 100 molecular proportions (Fig. 5, curves 2-7) causes further broadening of the absorption spectrum toward the region of longer wavelength by about 550 A, as compared to the absorption in ethanol.

The curve of the absorption spectrum obtained in the presence of 1000 molecular proportions of sulfuric acid (Fig. 6, curve 2) corresponds exactly with that obtained in ethanol. Upon increasing the amount of sulfuric acid to 10,000 molecular proportions, broadening of the absorption spectrum by 400 A toward the long waves is observed. After dilution the spectrum becomes the same as that of the solution in ethanol. Increasing the concentration of sulfuric acid to 17,000 molecular proportions (Fig. 6, curve 4) does not introduce any changes in the position of the absorption curve. After neutralization of sulfuric acid the solution exhibits an absorption spectrum analogous to that in ethanol (Fig. 6, curve 5).

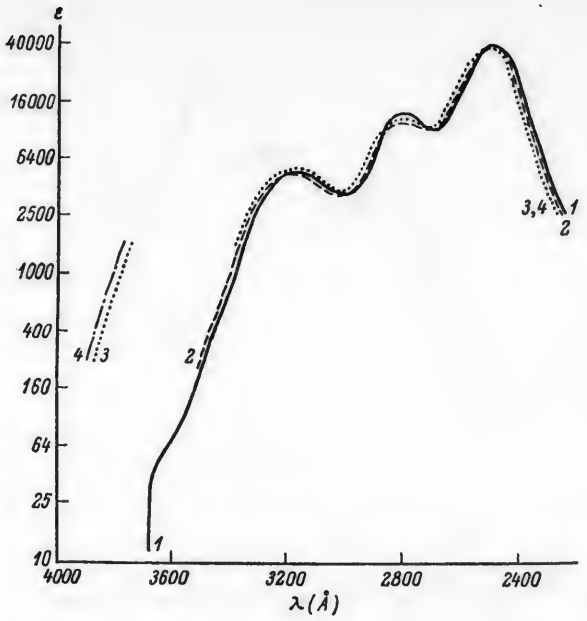


Fig. 6. Ultraviolet absorption spectra.
1) 1-Methoxy-3-hydroxy-4,6-diacetylbenzene in ethanol 10^{-2}-10^{-5} M; 2) the same + 1000 molecular proportions of H_2SO_4; 3) the same + 10,000 molecular proportions of H_2SO_4; 4) the same + + 17,000 molecular proportions of H_2SO_4.

Dimethyl ether of 1,3-dihydroxy-4,6-diacetylbenzene. The synthesis was based on Mouthner's method [4]. It was carried out without the use of solvent.

The absorption spectrum in ethanol (Fig. 7, curve 2) has bands at λ 3070 A (ε 6400), λ 2740 A (ε 26,000) and λ 2470 A (ε 35,480). The absorption of the dimethyl ether in ethanol is displaced toward the region of short wavelength by 300-350 A (Fig. 7, curves 1, 2), as compared to that of 1,3-dihydroxy-4,6-diacetylbenzene.

In ethanolic solutions of sulfuric acid the dimethyl ether was investigated in the presence of 100, 1000, 10,000 and 17,000 molecular proportions of the acid. The presence of 10,000 moles of sulfuric acid results in broadening of the absorption band toward the longer waves by 500 A (Fig. 7, curve 6). After dilution, absorption corresponding to a content of 100 molecular proportions of sulfuric acid is re-established (Fig. 7, curve 5). Increasing the amount of acid to 17,000 molecular proportions (Fig. 7, curve 7) does not change the absorption spectrum, but at a dimethyl ether concentration of about 10^{-3} M an absorption minimum appears at λ 2325 A (ε 1000) which evidently belongs to the spectrum of the products of reaction between sulfuric acid and the dimethyl ether. The absorption spectrum obtained after neutralization of the solution containing 17,000 molecular proportions of sulfuric acid (Fig. 7, curve 8) is the same as that obtained in ethanol.

Polarographic and Conductometric Investigation

The apparatus and method used in the polarographic and conductometric investigations were described previously [10]. In ethanolic solutions no oxidation-reduction reactions could be detected; and the investigation was therefore carried out in aqueous solutions; the insoluble dimethyl ether was not investigated.

In the investigation of 1,3-dihydroxy-4,6-diacetylbenzene the molar ratios of this substance to sodium hydroxide were 1 : 2, 1 : 4, 1 : 9, and the total concentration was $2 \cdot 10^{-2}$ M. The polarogram consists of two waves whose potentials depend upon the amount of sodium hydroxide (Table 1).

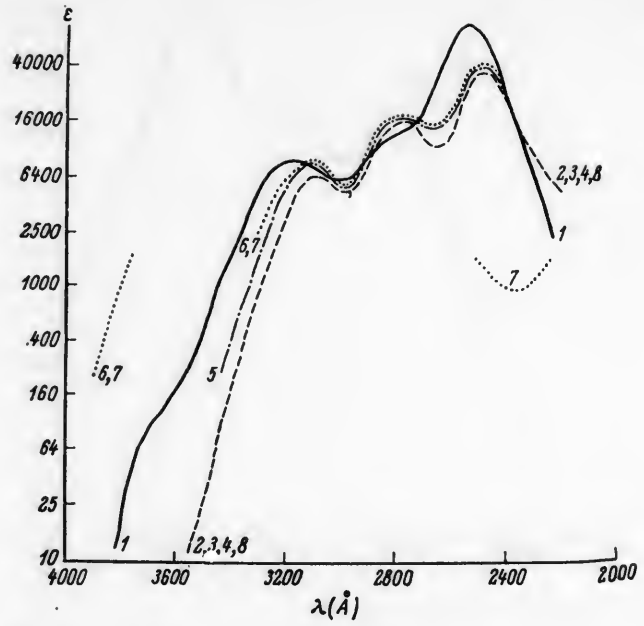


Fig. 7. Ultraviolet absorption spectra.
1) 1,3-Dihydroxy-4,6-diacetylbenzene in ethanol 10^{-2}-10^{-5} M; 2) 2,3-dimethoxy-4,6-diacetylbenzene in ethanol 10^{-2}-10^{-5} M; 3) the same + 1.0 molecular proportions of C_2H_5ONa; 4) the same + 100 molecular proportions of H_2SO_4; 5) the same + 1000 molecular proportions of H_2SO_4; 6) the same + 10,000 molecular proportions of H_2SO_4; 7) the same + 17,000 molecular proportions of H_2SO_4; 8) the same + 17,000 molecular proportions of H_2SO_4, after neutralization.

TABLE 1

Relation of the Reduction Potential of 1,3-Dihydroxy-4,6-diacetylbenzene to the Amount of Sodium Hydroxide

Concentrations of the system components (x 10^{-2} mole/liter)		Reduction potential in the region	
1,3-Dihydroxy 4,6-diacetyl-benzene	Sodium hydroxide	1.7—1.85 V	2.2—2.4 V
0.66	1.34	1.81	2.37
0.40	1.60	1.77	2.28
0.20	1.80	1.78	2.27

The curves of reduction potential against composition do not possess any singular points (Fig. 8).

The methyl ether of 1,3-dihydroxy-4,6-diacetylbenzene was investigated under the same conditions. The polarogram has one wave whose potential changes from 1.69 to 1.72 v when the sodium hydroxide content is increased from $1.34 \cdot 10^{-2}$ to $1.60 \cdot 10^{-2}$ M. At the $1.80 \cdot 10^{-2}$ M NaOH content the polarographic wave does not appear (Fig. 10).

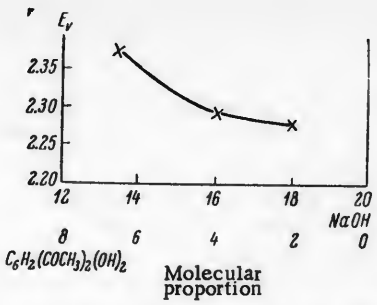


Fig. 8. Reduction potentials of the binary system 1,3-dihydroxy-4,6-diacetylbenzene-sodium hydroxide.

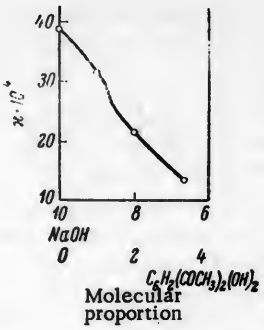


Fig. 9. Conductivity of the binary system 1,3-dihydroxy-4,6-diacetylbenzene–sodium hydroxide.

Conductometric investigation of 1,3-dihydroxy-4,6-diacetylbenzene was carried out at molar ratios to sodium hydroxide of 1 : 2, 1 : 4, 1 : 9 and at a total concentration of $2 \cdot 10^{-2}$ M (Fig. 9). With increase in the amount of sodium hydroxide, the conductivity increased to $27 \cdot 10^{-4}$ ohm^{-1} cm^{-1}. This increase is expressed by a section of the curve in the form of a hyperbola of large focal length. In the region of a molar ratio of 1 : 5.5 of 1,3-dihydroxy-4,6-diacetylbenzene to sodium hydroxide the curve exhibits a singular point. The hyperbola changes sign. Further increase in specific conductivity leads to the development of the curve in the form of a hyperbola of a large focal length, and the conductivity reaches the value $38 \cdot 10^{-4}$ ohm^{-1} cm^{-1}.

Discussion of Results

Because Morton and Stubbs [3] did not report in what solvent they carried out their investigation of 1,3-dihydroxy-4,6-diacetylbenzene, it is difficult to compare their results with those obtained in this investigation. The positions of the absorption maxima are given in Table 2.

TABLE 2

Solvent	Position of absorption maxima					
	Long-wave region		Medium ultraviolet region		Short-wave region	
	λ	ε	λ	ε	λ	ε
Isooctane	3240	12600	2700	40000	2520	151400
Ethanol	3180	8130	2750	16000	2520	79400
Reported by Morton and Stubbs [3]	3230	6166	2800	11760	2530	45710

A comparison indicates that their results [3] correspond most closely to the positions of absorption maxima in ethanolic solution. They differ from our results mainly in absorption intensity; the reason for this difference remains obscure. Analysis of results obtained by these authors with the dimethyl ether of 1,3-dihydroxy-4,6-diacetylbenzene leads one to surmise that they used ethanol as solvent (the authors mention its use for other substances). According to the results of this study the dimethyl ether is insoluble in isooctane. It is hard to believe that the ether can be dissolved in other hydrocarbon solvents. There is another important difference between the results obtained in this study and those reported by Morton and Stubbs: for 1,3-dihydroxy-4,6-diacetylbenzene we detected an additional weakly defined band, the maximum of which we tentatively place at λ 3550 A (ε 160).

The introduction of a second hydroxyl group into the molecule of 1,3-diacetylbenzene leads to still greater changes in the absorption spectrum when compared to that of 1-hydroxy-2,4-diacetylbenzene; the bands become less defined [5] (Figure 1, curve 2). The over-all intensity of the absorption spectrum of 1,3-dihydroxy-4,6-diacetylbenzene is considerably higher than that of 1-hydroxy-2,4-diacetyl benzene. The intensity of the

absorption band in the medium ultraviolet region is increased four-fold on account of the intramolecular hydrogen-bonding of two groups. Under the conditions of the investigation formation of intermolecular hydrogen bonds is excluded [6, 7].

Methylation of one hydroxyl group in 1,3-dihydroxy-4,6-diacetylbenzene causes only a two-fold decrease in the intensity of the band at λ 3180 A (Fig. 4, curves 1, 2). Methylation of a second hydroxyl group causes a displacement of the absorption bond at λ 3180 A toward the short-wave region by 130 A. (Fig. 7, curves 1, 2).

Calculation of the hydrogen-bond energy was done on the basis of the graphical expression of the Beer-Lambert-Schwartzschild law [11], and it was found to be 3.22 kcal/mole. Valiashko and Rozum [8] found that the hydrogen bond energy for o-hydroxyacetophenone was 8.253 kcal/mole. Introduction of a second acetyl group decreased the energy to 5.14 kcal/mole [11] because a para-conjugated system is formed; in the o-hydroxy-acetophenone molecule electron movement and consequently absorption were localized in an ortho-conjugated system with the participation of a hydrogen bond. Introduction of a second hydroxyl group intensifies the electron transitions in the molecule, and the influence of the hydrogen bond becomes less noticeable; its energy decreases to 3.22 kcal/mole. Attraction of electrons by the acetyl groups which disturbs the conjugated system of the benzene ring [5] is compensated by the noncovalent electrons of the hydroxyl groups. The vibration frequency decreases, and the whole absorption is displaced toward the long waves; i.e., into the region of lower energies.

Changes taking place in the electron system of 1,3-dihydroxy-4,6-diacetylbenzene can be followed much more completely with the aid of absorption spectra in ethanolic solutions of sodium ethoxide (Fig. 2, curves 2-7). Intensity of the absorption band at λ 3550A increases, possibly at the expense of broadening of the band at λ 3180 A, which depends on the ortho-conjugation of carbonyl and hydroxyl groups through the benzene ring. Development of absorption in the near-ultraviolet region leads to the lowering of absorption in the far ultraviolet region as a result of some displacement of the absorption center from a system of conjugated double bonds, in the ring to an ortho-conjugated system. Increasing the amount of sodium ethoxide changes the spectrum in a regular manner (Fig. 2, curves 2-7). The long-wave band extends still further into the long-wave region with almost no change in the position of the maximum. The absorption band at λ 2750 A becomes somewhat less intense and displaced toward the long-wave region. With the complete ionization of the 1,3-dihydroxy-4,6-diacetylbenzene molecule in an ethanolic solution of sodium ethoxide, almost all quantum states of the electron system become possible. Absorption approaches continuity (2 molecular proportions of ethoxide) (Fig. 2, curve 5). Ionization of hydroxyl groups leads to disruption of the hydrogen bonds, which to a certain degree favor localization of absorption in the ortho-conjugated system. Owing to the elimination of the conditions that isolate the ortho- and para-conjugated systems, the two types of conjugation become equally probable. Furthermore, under the influence of the alkalinity of the solvent (increase in dielectric constant) differentiation of electron-shifting in the molecule toward the functional groups develops all over again. In the spectrum it shows up in the development of absorption bands at λ 3550 (3000 A). The intensity of the first long-wave band, which develops as a result of increase in the absorption of the diacetylbenzene grouping and broadening of the band at λ 3180 A, and intensity of the second band in the middle ultraviolet region, which appears as the result of the displacement of absorption bands arising from the ortho- and para-conjugated systems, reach their highest values at 100 moles of sodium ethoxide per mole of 1,3-dihydroxy-4,6-diacetyl benzene (Fig. 2, curve 7). Merging of these two bands is due mainly to the displacement of absorption at λ 2700 A toward longer wavelength. The fact that upon increasing the amount of ethoxide from 0.1 to 0.2 molecular proportions (Fig. 2, curves 2-5) gradual, although only slight, displacement of this band into the long wavelength region can be observed supports such a hypothesis. Increasing the amount of ethoxide to 10 moles leads to a sudden displacement; 100 moles increases the displacement to a still greater extent (Fig. 2, curve 7). While investigating 2,4-dihydroxyacetophenone Valiashko and Rozum [9] discovered that the two corresponding absorption bands merge when the amount of sodium ethoxide is increased.

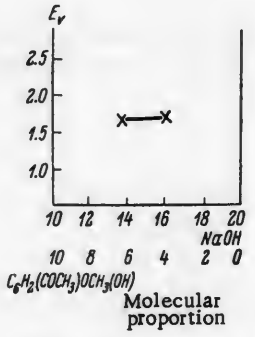


Fig. 10. Reduction potentials of the binary system: 1-methoxy-3-hydroxy-4,6-diacetyl-benzene—sodium hydroxide.

TABLE 3

Compounds	Reduction potential (volts)		
	First wave	Second wave	Third wave
1,3-Diacetylbenzene	1.24	1.74	2.58
1-Hydroxy-2,4-diacetylbenzene	1.54	1.89	2.27
1,3-Dihydroxy-4,6-diacetylbenzene	1.77	2.28	—
1-Methoxy-3-hydroxy-4,6-diacetylbenzene	1.72	—	—

Investigation of 1,3-dihydroxy-4,6-diacetylbenzene in ethanolic solutions of sulfuric acid (Fig. 3, curves 2-5) shows changes in the absorption spectrum which are analogous to those in the spectra of 1,3-diacetylbenzene and 1-hydroxy-2,4-diacetylbenzene and its methyl ether in the presence of sulfuric acid [10, 11]. The observed displacement of absorption into the long-wave region at 1000 mole of sulfuric acid per mole of 1,3-dihydroxy-4,6-diacetylbenzene (Fig. 3, curve 2) is equal to 250 A, and is somewhat smaller than that of 1-hydroxy-2,4-diacetylbenzene and 1,3-diacetylbenzene; in the case of 1,3-diacetylbenzene this displacement is 400 A and in the case of 1-hydroxy-2,4-diacetyl benzene it is 350 A [10, 11]. The smaller displacement of absorption in the case of the hydroxyl derivatives is the result of hydrogen bond formation which has the effect of reducing the influence of sulfuric acid on the electron system of the molecule during oxonium-salt formation.

In a comparison of the influence of methylation on the absorption spectra of hydroxy derivatives with the values of hydrogen bond energy, it can be assumed that the changes in the spectra are due to changes in the energy of electron system of the molecule resulting from hydrogen-bonding. Addition of varied amounts of sodium ethoxide (from 0.1 to 100 moles) (Fig. 5, curves 2-7) to the ethanolic solution of methyl ether of 1,3-dihydroxy-4,6-diacetylbenzene leads to a change in its absorption spectrum which is analogous to the changes in the spectra of 1,3-dihydroxy-4,6-diacetylbenzene and 1-hydroxy-2,4-diacetylbenzene [11]. 1-2 mole of ethoxide (Fig. 5, curves 4, 5) have less effect than in the case of 1,3-dihydroxy-4,6-diacetylbenzene because the ionization of only one hydroxyl group affords a smaller number of degrees of freedom. The absorption spectrum of 1,3-dimethoxy-4,6-diacetylbenzene in ethanolic solutions of sodium ethoxide does not change at all, because in this case no ionization of hydroxyl groups takes place (Fig. 7, curve 3).

With the introduction of hydroxy and methoxy groups into the molecule of 1,3-diacetyl benzene, singular points disappear on the curve for reduction potential as a function of composition. This lack of singular points is due to the influence of hydroxy and methoxy groups, which compensate for electron deficiency at the carbon atom of the carbonyl group. With the ionization of hydroxyl groups in an alkaline medium, electron displacements are still further facilitated. The values of reduction potentials presented in Table 3 were obtained for a ratio of components of 1 : 4 (Fig. 8, 10) [10, 11].

A comparison of spectrographic and polarographic data shows that there is a regular change in properties with change in the number of hydroxyl groups introduced. Introduction of hydroxyl groups increases the possibility of electron transitions, particularly in an alkaline medium. As a result, intramolecular interaction of functional groups increases and their intermolecular interactions and interactions with the solvent are suppressed. In the spectra these changes give rise to increased intensity of absorption bands and to equalization of the probabilities of absorptions by the ortho- and para- conjugated systems (Fig. 2). On the polarograms changes in functional-group composition lead not only to changes in reduction potentials (Table 3), but also to the gradual appearance of the third wave, which is very well defined in 1,3-diacetylbenzene [10]. In the monohydroxy derivative, its potential merely decreases but in the dihydroxy derivative the wave disappears completely (Fig. 8). Furthermore, increase in the number of hydroxyl groups with consequent decrease in intermolecular interaction is accompanied by the disappearance of the singular point on the composition–reduction potential curve (the presence of this point on the 1,3-diacetylbenzene curve was explained by the formation of a compound with sodium hydroxide [10]. All these changes give us grounds for the assumption that

the appearance of the third wave on the 1,3-diacetylbenzene curve [10] is due to oxidation-reduction reactions accompanying the replacement of intermolecular action of functional groups by intramolecular action.

Introduction of hydroxyl groups into the molecule of 1,3-diacetyl benzene leads, as previously mentioned, to decrease in the ability of the carbonyl group to react with sodium hydroxide. Although there is no singular point on the composition - reduction potential curve, such a point can be found on the composition - conductivity curve, though much vaguer than in the case of 1,3-diacetylbenzene. The vagueness is manifested not only in the smoothing out of the inflection, but also in its displacement toward higher concentrations of sodium hydroxide: in order that the reaction may take place almost double the equivalent amount of sodium hydroxide is necessary.

SUMMARY

1. 1,3-Dihydroxy-4,6-diacetylbenzene and its mono- and di-methyl ethers were investigated spectrographically in isooctane, ethanol, and ethanolic sodium ethoxide and sulfuric acid; and also polarographically in ethanolic and aqueous solutions in the presence of sodium hydroxide.

Conductometric investigation of 1,3-dihydroxy-4,6-diacetylbenzene was carried out in aqueous solution in presence of sodium hydroxide.

2. Presence of two intramolecular hydrogen bonds in 1,3-dihydroxy-4,6-diacetylbenzene was demonstrated and their energy was calculated.

3. It was found that 1,3-dihydroxy-4,6-diacetylbenzene forms an oxonium salt in sulfuric acid at concentrations above 50%.

4. It was established that regular changes in the reduction potential take place with the introduction of acetyl, hydroxyl and methoxy groups into the benzene ring.

5. Presence of singular points on the composition-reduction potential curves was explained by the influence of hydroxyl groups which decrease the reaction between carbonyl oxygen and sodium hydroxide.

LITERATURE CITED

[1] W. Bakker, J. Chem. Soc. 1934, 71.

[2] F. D. Chattaway, J. Chem. Soc. 1931, 2495.

[3] R. Morton, H. Stubbs, J. Chem. Soc. 1940, 1354.

[4] F. Mouthner, J. pr. Ch. 119, 311 (1928).

[5] N. Valiashko, and Yu. Rozum, J. Gen. Chem. 16, 593 (1946).

[6] V. Keussler, Z. Electroch. 58, 136 (1954).

[7] P. Borschewitz, Comptes rend. 237, 724 (1948).

[8] N. Valiashko, and Yu. Rozum, J. Gen. Chem. 17, 755 (1947).

[9] N. Valiashko and Yu. Rozum, ibid. 17, 783 (1947).

[10] F. Cheshko and B. Distanov, ibid. 27, 2183 (1957).*

[11] F. Cheshko and B. Distanov, ibid. 27, 2193 (1957).*

Received May 5, 1956

Kharkov Polytechnical Institute

* Original Russian pagination. See C. B. Translation.

CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXVI. CATALYTIC CONDENSATION OF COMPRESSED ACETYLENE WITH AROMATIC AMINES IN VAPOR PHASE

N. S. Kozlov and S. Ya. Chumakov

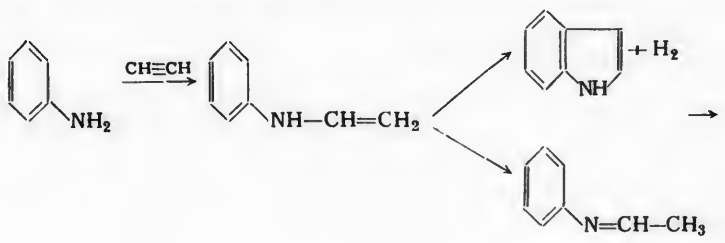
A. E. Chichibabin [1] was first to report that he was able to obtain indole, quinalidine and lepidine while passing aniline vapors in the current of acetylene through aluminum oxide heated to 360-420°, but no detailed account of the experiments was given. Japanese chemists Mijima, Unno and Ono [2] passed aniline vapors in the current of acetylene diluted with carbon dioxide through a porcelain tube heated to 600-700°. In the reaction products they found indole, quinoline, benzene, naphthalene etc. The yield of impure indole did not exceed 6% of the amount of aniline used in the reaction. Japanese chemists were more concerned with carbon dioxide, assuming that it takes plart in the reaction involving indole formation.

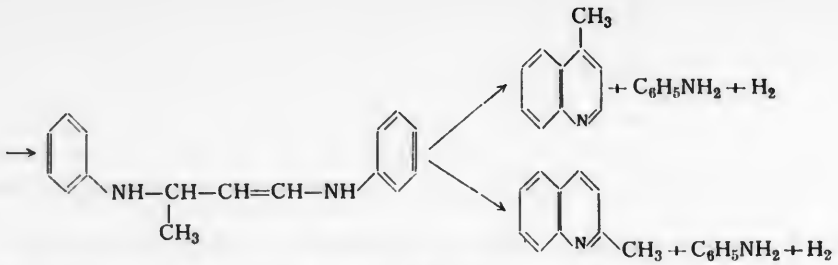
$$C_6H_5NH_2 + C_2H_2 + CO_2 = C_8H_7N + CO + H_2O$$

Later, this reaction received some attention in a number of foreign patents [3, 4] with various substances being tried as catalysts: zinc chloride on pumice, chromium oxide, silica gel and the like. According to the patent data, the yield of quinoline compounds reaches 50% of the aromatic amine entering into the reaction. Verifying some of the patent data the authors were able to establish that the yield of quinoline compounds did not exceed 6-8% of the amine used in the reaction.

Recently R. D. Obolentsev, Yu. N. Usov and Yu. V. Enkov [5] studied the reaction of catalytic condensation of acetylene with aniline over aluminosilicate catalyst heated to 450°. Quinaldine was found among the reaction products but its yield was small.

The authors decided to employ compressed acetylene for the condensation with amines, thinking that it should decidedly influence the course of the reaction. To the best of the authors' knowledge this type of work has not been tried up to the present time. Aluminum oxide, cuprous chloride on pumice and zinc acetate on pumice were tried as catalysts. All these substances proved to be extremely active catalysts for the investigated reaction. It was demonstrated that the use of compressed acetylene considerably increases the yield of the final products – quinoline and indole compounds. One must admit that reaction mechanism is extremely complex because, for example, quinaldine, lepidine and indole are formed in a reaction between acetylene and aniline over aluminum oxide. The authors suppose that the reaction takes place in the following manner:





Expressed presentations of reaction mechanism are confirmed by the data in the literature [6, 7]. The problem of lepidine formation remains obscure; possibly it is formed simultaneously with quinaldine, although the possibility of its formation through isomerization of quinaldine should not be excluded. This problem is being investigated at present.

EXPERIMENTAL

A somewhat improved apparatus previously described in a work by one of the authors [8] was used to carry out the reaction.

The following were tried as catalysts: domestic activated aluminum oxide which was used in the form of pieces, 3-5 mm in diameter; the apparatus was charged with a portion of the catalyst weighing 40 g and occupying 50 ml; cuprous chloride on pumice; the portion of the catalyst weighed 20-25 g, had a volume of 50 ml and contained 2-3 g of cuprous chloride. Upon the completion of the experiment it was discovered that copper acetylide instead of cuprous chloride was left on the pumice. This transformation of cuprous chloride into copper acetylide during reactions of acetylene with aromatic amines in liquid phase was previously discovered by one of the authors [9].

As a rule, in working with acetylene one tries to avoid the formation of copper acetylide which, it is generally known, exhibits explosive properties. It is also known that copper acetylide is employed as a catalyst in the commercial preparation of butanediol from formaldehyde and acetylene [10]. It is known that copper acetylide looses its explosive properties when deposited on an inert carrier [11]. It has been also established that copper acetylide appears to be less explosive in an atmosphere of acetylene than in air [12]. In the conducted experiments no explosions occurred despite the formation of copper acetylide in the reaction vessel. Finally, pumice impregnated with zinc acetate was tried as the catalyst. The catalyst portion weighed 20-25 g, had a volume of 50 ml and contained 2-3 g of the salt.

A description of one experiment is given as an example. 25 g of aniline was passed with the rate of 10 drops per minute over aluminum oxide heated to 300-310°. During the experiment acetylene pressure in the apparatus was maintained at 10-12 atm. The following fractions were obtained upon distillation of the catalyzate: 1st, 70-190°, 1 g; 2nd, 190-200°, 5.5 g; 3rd, 200-260°, 20 g; residue, 1 g. Benzene which was formed from aniline was found in the 1st fraction, while in an experiment with p-toluidine only toluene was found. 2nd fraction was composed of aniline with admixture of quinoline compounds. The product in the 3rd fraction was worked-up with 10% HCl. The insoluble part was extracted with ether. 10 g of quinaldine b. p. 245-250°, d_4^{20} 1.060, picrate m. p. 191° was obtained from the hydrochloric acid solution upon diazotization. No melting point depression was observed when mixed melting point was taken with quinaldine picrate. In addition to quinaldine 2 g of quinoline compounds b. p. 250-265° was also obtained. Their picrate melted at 210°. A mixture of the picrate with lepidine picrate showed no melting point depression.

After the removal of ether from the ether extract containing products insoluble in 10% HCl, the extract was subjected to distillation during which 5 g of a product with b. p. 240-260° was obtained. Upon standing, crystals with m. p. 52-54° separated out, their picrate melted at 184-185°; the substance gave a positive color test for indole with a pine splinter. It was determined by the picrate method that the product of fraction with b. p. 240-260° contained about 50% of indole. Therefore, if one assumes that the product of the 2nd fraction with b. p. 190-200° is exclusively aniline, then the yield of quinaldine calculated on the basis of aniline entering into the reaction is 32.8% and of indole 10%. Results of subsequent experiments are presented in the table.

Amine	Catalyst	Temperature of the experiment	Acetylene pressure (atm)	Yield of quinoline compounds (%)		Yield of indole (%)	
				on the basis of amt. of amine used	on the basis of amt. of amine entering into react.	on the basis of amt of amine used	on the basis of amine entering into react.
Aniline	Aluminum oxide	300—310°	1	5	—	Traces	Traces
"	The same	300—310	5	13.0	25.0	—	3.0
"	"	300—310	10—12	26.0	32.8	—	10.0
p-Toluidine	"	300—310	10—12	—	20.4	Traces	—
Aniline	Cuprous chloride	250—260	10—12	29.3	33.0	5.7	7.2
"	Zinc acetate	230—240	1	Traces	Traces	None	None
"	The same	230—240	10—12	16.3	32.6	"	"
m-Toluidine	"	230—240	10—12	27.4	33.0	"	"
p-Toluidine	"	230—240	10—12	27.4	31.4	"	"

Data of the reported experiments show that the tested catalysts possess definite specificity of action. Thus under the influence of aluminum oxide and copper acetylide, indole, quinaldine and lepidine are formed from aniline and acetylene, while under the influence of zinc acetate and under the same experimental conditions indole is not formed at all, and lepidine is formed in negligible amounts.

SUMMARY

1. Reaction of catalytic condensation of acetylene compressed to 10-12 atm with primary aromatic amines in vapor phase was studied. Aluminum oxide, cuprous chloride and zinc acetate were tried as catalysts.

2. It was established that the use of compressed acetylene significantly increases yields of final reaction products – quinoline and indole compounds.

LITERATURE CITED

[1] Chichibabin, A. E., J. Russ. Chem. Soc. 47, 703, 1915.

[2] Ber. 55, 3854 (1922).

[3] Fogel, I. G., Acetylene. Leningrad, 297, 1934.*

[4] Newland, J. and Vogt, R., Acetylene Chemistry, Foreign Lit. Press, 247, 1947.**

[5] Obolentsev, R. D., Usov, Yu. N. and Enkov, Yu. V., J. Gen. Chem. 24, 254, 1954.***

[6] Amer. pat. 1804229, 1931.

[7] Ardashev, B. I., Prog. Chem. 23, 45, 1954.

[8] Kozlov, N. S., Friedman, G. E. and Volchkova, V. P., Trudy Inst. Chem. Acad. Sci. BSSR, 3, 5, 1937.

[9] Kozlov, N. S. and Fedoseev, P. N., J. Gen. Chem. 6, 250, 1936.

[10] Collection, Acetylene Chemistry, Foreign Lit. Press, 284, 1954.**

[11] Amer. pat. 2521424, 1950.

[12] Komovsky, N., J. Appl. Chem. 3, 401, 1930.

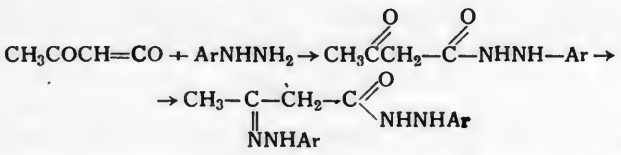
Received June 10, 1956

*In Russian.
**Russian translation.
***Original Russian pagination. See C. B. Translation.

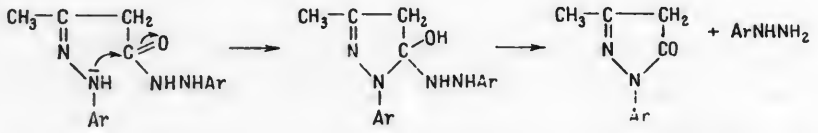
SYNTHESIS OF 1-(4'-SULFOPHENYL-3)-3-METHYLPYRAZOLONE-5 FROM DIKETENE AND 4-SULFONOPHENYLHYDRAZINE

P. A. Levin

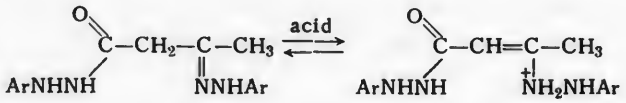
Aryl hydrazines are easily acylated by diketene. The reaction can proceed further with the formation of aryl hydrazone by acetoacetic acid aryl hydrazide, which under proper conditions splits off a molecule of aryl hydrazine and closes the pyrazolone ring. Initially, acetoacetic acid aryl hydrazide is formed from aryl hydrazine and diketene. The synthesis is usually carried out slowly, by adding diketene to aryl hydrazine. Under these conditions (large excess of aryl hydrazine) formation of the hydrazone proceeds



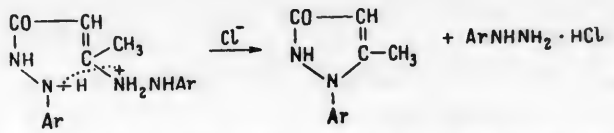
Upon heating and action of certain reagents, C=O bond of aryl hydrazone of acetoacetic acid aryl hydrazide, possessing considerable polarity, becomes further polarized to the point when pulling of electrons away from the C-atom creates a possibility for the unshared pair of electrons of the hydrazone nitrogen located at Ar to enter into the formation of a new bond N–C; hydrogen acquires mobility and shifts from nitrogen to oxygen. The oxy-compound thus formed immediately decomposes with the formation of 1-aryl-3-methylpyrazolone-5 and liberation of an aryl hydrazine molecule, which takes part in a new cycle of transformations.



Upon heating in the presence of acids the reaction proceeds through a different path: possibly partial or total transformation of aryl hydrazone of acetoacetic acid from the hydrazone form to the imine form takes place.



Activity of the remaining unshared pair of electrons of the hydrazoneimino group decreases; besides, conditions arise favoring the displacement of electron density from carbon atom 3 to oxygen and nitrogen. As a result, ring closure of isomeric pyrazolone-3 takes place:



In this manner 1-phenyl-5-methylpyrazolone-3 and some of its derivatives were obtained in 90-95% yields [1], while other methods did not give over 65% yields [2, 3].

In the formation of a pyrazolone-5 ring the condensing agent is diketene, but strong acetic acid, phenylhydrazine, alkali or dry hydrogen chloride can be used [4]. Heating of phenylhydrazine, 2,4-dinitrophenylhydrazine, m- and p-tolylhydrazine with diketene in benzene or toluene allowed us to obtain corresponding pyrazolones [5].

Use of hydrocarbons as the reaction medium hampers the synthesis of sulfono-, carboxy- and some other pyrazolones. In this study an attempt was made to synthesize 1-(4'-sulfonophenyl)-3-methypyrazolone-5 by carrying out the reaction in an aqueous medium.

EXPERIMENTAL

Suspension of 4.3 g (0.02 mole) of 4-sulfonophenylhydrazine in 40 ml of water was stirred with 2.1 ml (0.022 mole) in diketene for 2 hours at temperature not exceeding 12°. Stirring was continued for additional 1.5 hours at 60-70°. Upon cooling, a white microcrystalline precipitate separated out from the reaction mixture. The product was analyzed by the nitrosation method. It represented 98.6% 1-(4'-sulfonophenyl)-3-methylpyrazolone-5. Yield 2.2 g (40%, based on sulfonophenylhydrazine). According to nitrometric analysis the filtrate contained 0.46 g of sulfonophenylhydrazine (12.3% of starting amount).

5.3 ml (0.055 mole) of diketene was added dropwise to 9.7 g (0.05 mole) of sulfonophenylhydrazine in 150 ml of water. The mixture was stirred with cooling for 4 hours. On the following day a pink crystalline precipitate was filtered off. It was washed with cold water and dried at 50°; weight 7.5 g. The precipitate contained 67.2% of sulfonophenylhydrazine as determined nitrometrically (decomposition with freshly precipitated hydrated copper oxide). It also contained intermediate reaction products and 25% of sulfonophenylmethylpyrazolone. 2.1 g of sulfonophenylmethylpyrazolone together with decomposition products of sulfonophenylhydrazine was contained in the filtrate. Total yield of sulfonophenylmethylpyrazolone 31.1%, which included 14.8% contained in the precipitate. 53.6% of sulfonophenylhydrazine did not enter into the reaction.

If in an analogous experiment the mixture was heated for 2 hours (75-80°) after the 4-hour stirring period, a white precipitate representing 94% sulfonophenylmethylpyrazolone separated out. Yield 36.7%. The filtrate contained sulfonophenylhydrazine.

The mixture which formed after a 4-hour stirring period of diketene with a suspension of 9.7 g of sulfonophenylhydrazine was dried. 11 g of a yellowish fluffy powder was obtained. Gasometric analysis gave 22.4% of sulfonophenylhydrazine in the product, sulfonophenylmethylpyrazolone content 57.2% as determined by nitrosation (weight of sample 0.3020 g; used 10.80 ml of 0.1 N sodium nitrite after the removal of sulfonophenylhydrazine). Yield of sulfonophenylmethylpyrazolone 49.5%, 26.2% of sulfonophenylhydrazine remained, 24.3% of the latter decomposed. A similar method of obtaining sulfonophenylmethylpyrazolone in paste form was described in one of the surveys on diketene [6]. The reported 80% yield is probably somewhat high as a result of inaccurate analysis of the obtained product by means of benzenediazonium chloride. The latter is capable of entering into a reaction not only with pyrazolone but also with sulfonophenylhydrazine and with intermediate products of the reaction [7].

SUMMARY

Diketene is capable of entering into a reaction with sulfonophenylhydrazine in an aqueous medium, the final product of the reaction being 1-(4'-sulfonophenyl)-3-methylpyrazolone-5 in 40% yield (not considering its content in the filtrate) and of good quality (98.6%).

When the synthesis is carried out without heating, with insufficient heating or with drying of the reaction mixture, the final yield is lower and the quality of the product poorer.

LITERATURE CITED

[1] Amer. pat. 2227654, 1940.

[2] Lehrer, J. pr. ch. [2], 45, 90 (1892); Meyer, Ber. 36, 717 (1903).

[3] A. Michaelis, Lieb. Ann. 338, 267 (1905).

[4] H. Z. Lecher et al., J. Am. Chem. Soc. 66, 1959 (1944).

[5] German pat. 637260, 1935.

[6] A. B. Boese, Ind. Eng. Ch. 32, 16 (1940).

[7] K. Saunders, Aromatic Diazocompounds and Their Technical Application,* Moscow, pp. 173-176, 1938.*

Received August 30, 1956

K. E. Voroshilov Intermediate Product and Dye Research Institute, Leningrad Branch

*In Russian.

CONDENSATION OF PROPYLENE OXIDE WITH SOME AROMATIC HYDROCARBONS

V. R. Likhterov and V. S. Etlis

The condensations of olefin 1,2-oxides with aromatic hydrocarbons have been studied relatively little. The condensations of ethylene oxides with aromatic compounds have been studied more thoroughly [1-3]. It was shown that under certain conditions, in the presence of $AlCl_3$, ethylene oxide and benzene will give β-phenylethyl alcohol in 45% yield. On condensing propylene oxide with benzene, methyl benzylcarbinol was obtained as a side product in 8% yield [2]. This alcohol may be prepared from phenylmagnesium bromide and propylene oxide [4] in ether in 60% yield (calculated on the propylene oxide), by reducing benzyl methyl ketone [5], from benzyl bromide and paraldehyde through an organomagnesium compound [6] or from styrene oxide and methylmagnesium iodide [7]. All these methods are quite complicated and give low yields of the required product.

It seemed interesting to study in greater detail the condensation of propylene oxide with aromatic hydrocarbons in the presence of anhydrous aluminum chloride in order to obtain aliphatic-aromatic alcohols.

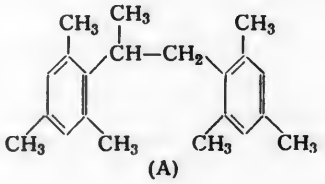
In investigating condensations of propylene oxide with benzene, we studied the effects of temperature, amount of $AlCl_3$ and excess benzene.

Having established the optimal conditions for reacting propylene oxide with benzene, we turned to the study of its condensation with other aromatic compounds. Thus, with toluene it gave a mixture of isomeric 1-tolylpropanols-2 in 41% yield, which was analyzed by oxidation, conversion of the resulting phthalic acids to the methyl ethers and separation of the latter [3]. It was established that the composition of the alcohol mixture obtained was approximately the following: 51% o-isomer and 49% p-isomer.

Condensation of propylene oxide with p-xylene gave 1-(2,5-dimethylphenyl)-propanol-2 in 28.5% yield.

With mesitylene we obtained 1-(2,4,6-trimethylphenyl)-propanol-2 in 7.0% yield, while the main reaction product was a hydrocarbon, $C_{21}H_{28}$, apparently of structure A.*

Condensation of propylene oxide with anisole gave a mixture of isomeric 1-methoxyphenyl-2-propanols in 20.3% yield. In addition to them, a product, $C_{17}H_{20}O_2$, was isolated in 18.2% yield which was, apparently, a mixture of isomeric 1,2-dianisylpropanes.



(A)

EXPERIMENTAL

The propylene oxide used had b.p. 34.5-35.0°, n_D^{20} 1.3670, d_4^{20} 0.8399. Condensation of propylene oxide with aromatic hydrocarbons was performed in a liter, four-necked, pear-shaped flask, fitted with a mechanical stirrer, a reflux condenser, a thermometer and a dropping funnel, cooled in ice. Nitrogen was introduced through a tube, leading in through the condenser. The whole system was carefully protected from atmospheric moisture. In all cases, the same procedure was used: a solution of propylene oxide in the hydrocarbon was added dropwise to a vigorously stirred suspension of $AlCl_3$ in the aromatic hydrocarbon, cooled externally with ice. During the addition, nitrogen was passed in at a rate of 30-40 bubbles a minute. At the end of the addition, the mixture was stirred for 1 hour at room temperature and then poured into dilute hydrochloric

* This structure is proposed in analogy with the hydrocarbon obtained by condensing propylene oxide with benzene [2].

TABLE 1

Conditions of the Condensation of Propylene Oxide (33 g) with Benzene

Experiment No.	Charge		Temperature	Yield of methylbenzylcarbinol (in %)
	Benzene* (in ml)	$AlCl_3$ (in g)		
1	515	76	5°	30
2	515	114	5	30
3	515	76	33—38	6 (+20% 1,2-diphenylpropane)
4**	515	76	5	37
5***	515	76	5	41
6***	258	76	5	25

* Counting the benzene taken to dissolve the propylene oxide.

** Before adding the propylene oxide, the mixture was flushed with dry nitrogen.

*** The experiment was carried out with dry nitrogen passing through.

TABLE 2

Conditions of the Condensation of Propylene Oxide with Benzene Derivatives at 5°

Name of compound	Charge			Length of experiment (in hours)	Names of main reaction products	Yield (in %)
	aromatic compound (in ml)*	propylene oxide (in g)	$AlCl_3$ (in g)			
Toluene	605	33	76	3	1-(Methylphenyl)-propanol-2	41.0
p-Xylene	385	18.1	41.7	2	1-(2,5-Dimethylphenyl)-propanol-2	28.0
Mesitylene	336	14	33.2	2	1-(2,4,6-Trimethylphenyl)-propanol-2	7
					1,2-di-(2,4,6-trimethylphenyl)-propane	30
Anisole	209	11.2	25.7	1.5	1-(Methoxyphenyl)-propanol-2	20
					1,2-di-(Methoxyphenyl)-propane	18

* Counting that used to dissolve the propylene oxide.

acid and ice; the hydrocarbon layer was separated, washed and dried over potassium carbonate. After distilling off the excess of the starting aromatic hydrocarbon, the residue was distilled in vacuum. After the distillation, a small amount of tarry products was always left in the flask.

The results are given in the table.

As the data in Table 1 show, at 33-38° the main reaction product was 1,2-diphenylpropane. Under these conditions hardly any alcohol was formed. Excess benzene favored the yield of alcohol and the best results (Experiment 5) were obtained with a 10 mole excess of benzene. In all cases the amount of $AlCl_3$ had to be less than 1 mole per mole of propylene oxide. To improve the yield of carbinol, the reaction mixture was flushed out with dry nitrogen, possibly to remove hydrogen chloride formed. The latter could react with propylene oxide to form propylene chlorohydrin. As our experiments showed, under the given conditions, propylene chlorohydrin does not condense with benzene and therefore HCl could sharply decrease the yield of alcohol.

The 3,5-dinitrobenzoate of methylbenzylcarbinol had m.p. 62.5°. A mixture of the 3,5-dinitrobenzoate of the carbinol prepared from phenylmagnesium bromide and propylene oxide melted without depression.

Oxidation of the mixture of isomeric methyltolylcarbinols. In a liter flask with a reflux condenser was placed 400 ml of water, 30 ml of 30% NaOH and 16.7 g of alcohol and the mixture heated to boiling, after which $KMnO_4$ (135 g, 20% excess compared with the theoretical) was added little by little. After 15 hours boiling, the mixture was cooled and the precipitate of MnO_2 filtered off. The filtrate was evaporated down to

TABLE 3

Physicochemical Properties of the Products Isolated

Product name	Boiling point (pressure in mm)	Specific gravity		Refractive index		Molecular refraction MR_D		Elementary analysis (in %)			
								found		calculated	
		d_4^{20}	literature data	n_D^{20}	literature data	found	calculated	C	H	C	H
1-Phenylpropanol-2 ($C_9H_{12}O$)	92(2)	1.0021	1.1091(16°)	1.5210	1.5628(16°)[8]	41.4	41.6	78.85	8.89	79.40	8.82
1-(Methylphenyl)-propanol-2 ($C_{10}H_{14}O$)	97(2)	0.9780	—	1.5176	—	46.4	46.3	80.07	10.10	80.00	9.33
1-(2,5-Dimethylphenyl)-propanol-2 ($C_{11}H_{16}O$)	112(3)	0.9781	0.9865(21°)	1.5214	1.5191(21°)[9]	50.9	50.92	80.09	9.38	80.50	9.75
1-(2,4,6-Trimethylphenyl)-propanol-2 ($C_{12}H_{18}O$)	122(3)	0.9778	—	1.5286	—	56.0	55.5	80.43	10.13	80.90	10.10
1,2-Di-(2,4,6-trimethylphenyl)-propane ($C_{21}H_{28}$) *	175(3)	0.9660	—	1.5493	—	91.8	92.0	90.10	10.10	90.00	10.00
1-(Methoxyphenyl)-propanol-2 ($C_{10}H_{14}O_2$)	121(3)	1.0441	—	1.5272	1.5261(25°)[10] p-isomer	48.5	48.0	71.95	8.45	72.30	8.43
1,2-Di-(methoxyphenyl)-propane ($C_{17}H_{20}O_2$)**	180(3)	1.0690	—	1.5629	—	77.5	76.8	76.01	8.33	75.70	8.74

* M 273 (by Rast's method); M 280 Picrate: m. p. 118°

** M 245 (by Rast's method); M 256 Picrate: m. p. 117.5-118.5°.

800 ml and made very acid to methyl orange with H_2SO_4. After cooling the product to 15°, we collected the precipitate A, which was washed 3 times with boiling water (50 ml each). The residue was dried at 100° and weighed 5.93 g. The acid filtrate and the wash water were evaporated down to 900 ml and the o-phthalic acid extracted with ether (14 times with 100 ml). Then the mother liquors were evaporated down to 300 ml and extracted 3 more times with 200 ml of ether. All the ether extracts were combined and the ether distilled off. The residue weighed 6.2 g and after recrystallizing it from water, we obtained pure o-phthalic acid with m.p. 176° (in a sealed capillary).

4 g of precipitate A was heated with 25 ml of CH_3OH and 4 g of H_2SO_4 at 80° for 70 minutes and then the mixture was neutralized with a solution of $NaHCO_3$ and the m-phthalate extracted with ether (3 times with 50 ml each). After distilling off the ether there was no solid residue; consequently, m-phthalic acid was absent. 5.93 g of p-phthalic acid was obtained. If we assume that all three isomers are oxidized equally easily, then the original carbinol consisted of a mixture of 51% of 1-(2-methylphenyl)-propanol-2 and 49% of 1-(4-methylphenyl)-propanol-2.

SUMMARY

1. We investigated the condensation of propylene oxide with benzene, toluene, p-xylene, mesitylene and anisole in the presence of $AlCl_3$ and isolated the main reaction products.

2. We established the optimal conditions for 1-phenylpropanol-2 formation.

LITERATURE CITED

[1] A. Schaarschmidt, L. Hermann and B.Szemzö, Ber. 58, 1914 (1925).

[2] R. A. Smith and S. Natelson, J. Am. Chem. Soc. 53, 3476 (1931).

[3] J. Colonge, and P. Rochas, Bull. Soc. Chim. No. 7-8, 819 (1948).

[4] M. S. Newman, J. Am. Chem. Soc. 62, 2295 (1940).

[5] H. Phillips, J. Chem. Soc. 123, 22 (1923).

[6] Tiffeneau and T. Delange, Comptes rend. 137, 575 (1903).

[7] C. Golumbic, and D. L. Cottle, J. Am. Chem. Soc. 61, 996 (1939).

[8] Dictionary of Org. Compounds, Foreign Lit. Press (1949).*

[9] G. Francais, Ann. Chim. 11, 212 (1939).

[10] S. Winstein, and B. K. Morse et al., J. Am. Chem. Soc. 74, 1113 (1952).

Received October 22, 1956

* Russian translation.

SYNTHESIS OF α,β-DIMERCAPTOPROPIONIC ACID, CONTAINING RADIOACTIVE SULFUR

A. B. Silaev, An. N. Nesmeyanov, V. M. Fedoseev and N. V. Kondakova

As is known, many sulfur-containing organic compounds play an important role in the biochemistry of animal organisms and may be used for therapeutic purposes. Thus, 2,3-dimercaptopropanol (BAL) is used as a remedy for lewisite and heavy metal poisoning. Some BAL derivatives (glucoside and esters) and compounds similar to them in structure have been found more effective therapeutically. It is possible that this is due to their high chemical stability. For example, α,β-dimercaptopropionic acid $CH_2(SH)CH(SH)COOH$ is 2.5 times more stable to oxidation with atmospheric air than BAL [1].

To investigate the distribution of thiols and dithiols in an organism, and the length of their biological lives, compounds labeled with radioactive sulfur are used. In this work we describe the preparation of dimercaptopropionic acid with the radioactive sulfur isotope S^{35}.

There is no description in the literature of dimercaptopropionic acid labeled with sulfur. The American patent [2] proposed a method of preparing the inactive acid by the addition of thioacetic acid at the unsaturated bond followed by substitution of the chlorine in the methyl ester of α-chloroacrylic acid.

$$CH_2{=}CClCOOCH_3 \xrightarrow{CH_3COSH} CH_2(SCOCH_3)CHClCOOCH_3 \longrightarrow$$
$$\xrightarrow{CH_3COSH} CH_2(SCOCH_3)CH(SCOCH_3)COOCH_3 \xrightarrow[\text{alcohol}]{1\%\ HCl}$$
$$\longrightarrow CH_2(SH)CH(SH)COOCH_3 \xrightarrow[\text{water}]{1\%\ HCl} CH_2(SH)CH(SH)COOH$$

The yield of dimercaptopropionic acid did not exceed 30%, calculated on the starting compound. This procedure was proposed as a general method for synthesizing a new class of compounds – dimercaptocarboxylic acids and their esters.

We prepared labeled dimercaptopropionic acid by the simpler and easier method of direct sulfohydrogenation of dibromopropionic acid with sodium hydrosulfite. This method gave good results in the synthesis of dimercaptopropanol and its ethers.

American authors [3] note that in preparing dimercaptopropionic acid by direct sulfohydrogenation, an inseparable mixture of substances with low sulfur content is formed.

We showed that by selecting suitable conditions, α,β-dimercaptopropionic acid may be prepared in good yields by the scheme

$$CH_2BrCHBrCOOH \xrightarrow[CH_3OH]{NaSH} CH_2(SNa)CH(SNa)COONa \xrightarrow{HCl} CH_2(SH)CH(SH)COOH.$$

These conditions are: dilution of the reaction mixture with methanol, a moderate temperature during the reaction, all operations carried out in a stream of nitrogen and high vacuum during distillation of the reaction product mixture.

EXPERIMENTAL

Preparation of dibromopropionic acid. By bromination of allyl alcohol in ether we obtained dibromopropyl alcohol in 90% yield. Oxidation of this with hot nitric acid (d 1.47) gave a 73% yield of dibromopropionic acid with m.p. 62-63° (62-64° [4]).

Preparation of sodium hydrosulfide with S^{35}. In the work we used the radioactive isotope of sulfur, S^{35}, with a half-life of 87 days. Radioactive hydrogen sulfide was prepared by decomposing active sodium sulfide with hydrochloric acid or by melting elementary radioactive sulfur with a mixture of asbestos and paraffin.

Dry hydrogen sulfide was absorbed in a cooled solution of 50 g (2.12 mole) of pure metallic sodium in 1 liter of methyl alcohol. When the evolution of radioactive hydrogen sulfide ceased, hydrogen sulfide was passed through the system from a Kipps apparatus until saturation. The methanol solution of sodium hydrosulfide obtained had a total activity of ~40 mC.

Preparation of dimercaptopropionic acid. To the solution of sodium hydrosulfide obtained was added 90 g (0.39 mole) of dibromopropionic acid and the mixture stirred and poured into three thick walled bottles (800 ml each), which were filled to the top, tightly closed and left at room temperature for 10 days. After this they were opened, the mixture made weakly acid to congo with concentrated hydrochloric acid and the solution remaining after separation of the inorganic salts, evaporated in a stream of nitrogen to 300-350 ml. The temperature of the water bath did not rise above 60°. The residue was diluted approximately twice with distilled water and the oil, which separated, extracted with 100 ml of ether. Extraction was continued until new portions of ether ceased to give a positive reaction for SH groups (only traces of color on treatment with an acid solution of sodium nitrite).

The combined ether extracts were dried with sodium sulfate and evaporated in a stream of nitrogen. The residue was a thick yellow oil, which crystallized only on long standing and therefore we identified the pure dimercaptopropionic acid from the mixture by distillation in a current of nitrogen under reduced pressure ($6 \cdot 10^{-3}$-$8 \cdot 10^{-3}$ mm). At first we distilled off 12 g of methyl dimercaptopropionate with b.p. 45° (0.1 mm) and n_D^{25} 1.5227 (according to data [2] n_D^{25} 1.5251); then we collected an acid with b.p. 60° (0.025 mm), which crystallized in the receiver. The crystals were slightly yellowish. The yield was 30 g (30%). On recrystallization from chloroform, the snow-white crystals with a weak smell had m.p. 72-73° (literature data 74-74.5° [2]).

Found* %: SH 48.00. $C_3H_6O_2S_2$. Calculated 47.86.

The specific activity of the dimercaptopropionic acid obtained was $2.5 \cdot 10^5$ counts/min per gram. The yield of the acid may be increased by hydrolysis of the reaction side product – methyl dimercaptopropionate.

The sodium salt of dimercaptopropionic acid. A sample of the acid was dissolved in anhydrous methyl alcohol and the calculated amount of sodium hydroxide (chemically pure) was added to the solution. The solution was evaporated to dryness in vacuum and treated with ether. The salt obtained was a white crystalline material, soluble in water, alcohol, hot acetone and dioxane and insoluble in ether and chloroform.

Found %: SH 41.65. $C_3H_5O_2S_2Na$. Calculated %: SH 41.29.

Isotopic exchange of sulfur between dimercaptopropionic acid and sodium hydrosulfide. In order to determine whether or not an isotopic exchange of sulfur occurred between dimercaptopropionic acid and sodium hydrosulfide in methanol solution, 0.4 g (0.007 mole) of sodium hydrosulfide, containing S^{35} (crystalline hydrosulfide was obtained from concentrated alcohol solution by adding cold absolute ether), was added to a solution of 2.9584 g (0.02 mole) of inactive dimercaptopropionic acid in methyl alcohol, neutralized with 0.87 g of sodium hydroxide. The mixture was diluted to 125 ml with methyl alcohol and placed in a flask with a reflux condenser, which was put into a thermostat at 55 ± 1°. Samples were taken immediately after mixing the components and after 18 hours. The degree of exchange was determined by the activity of the organic fraction. The samples taken (5 ml) were acidified with 0.5 ml of concentrated hydrochloric acid and the hydrogen sulfide liberated was sucked off with a water pump and adsorbed in alkali. The dimercaptopropionic acid was oxidized to

* The analysis for the SH group was carried out by the method developed by A. P. Terentyev, S. I. Obtemperanskaya and M. M. Buzlanova in the organic analysis laboratory of Moscow State University Chemistry Faculty (the determination of the active hydrogen in the SH group with acrylonitrile).

sulfuric acid by Messinger's method [5], namely, boiling for 2 hours with alkaline permanganate and subsequently adding hydrochloric acid.

The sulfate ion was precipitated as barium sulfate, which was precipitated in demountable steel beakers onto thin aluminum discs and measured with an end-window counter. After 18 hours the activity of the dimercaptopropionic acid had not changed from the activity of a blank sample, i.e., under the given conditions there was no isotopic exchange.

SUMMARY

We put forward a method for synthesizing α,β-dimercaptopropionic acid by direct sulfohydrogenation of dibromopropionic acid. The acid, containing radioactive sulfur, was prepared by this method. We showed the absence of isotopic exchange between the sodium salt of dimercaptopropionic acid and sodium hydrosulfite at a temperature of 55° for 18 hours in a methanol medium.

LITERATURE CITED

[1] E. S. G. Barron, Z. B. Miller and G. Kalnitsky, Biochem. J. 41, 62 (1947).

[2] U. S. Pat. 2422246; Ch. A., 41, 6277 (1947).

[3] A. A. Pavlic, W. A. Lazier, F. K. Signaigo, J. Org. Ch. 14, 59 (1949).

[4] G. Münder and B. Tollens, Lieb. Ann. 167, 227 (1873).

[5] J. Messinger, Ber. 21, 2914 (1888).

Received October 22, 1956

Moscow State University

SYNTHESIS OF DIETHYLAMINOETHANOL, LABELED WITH RADIOCARBON C^{14} IN ONE OF THE ETHYL GROUPS

L. B. Dashkevich

The esters of some carboxylic acids (benzoic, paraaminobenzoic, diphenylacetic, etc.) and diethylaminoethanol are effective medicines, which are widely used in medical practice. As the use of the "labeled atoms" method may give a fuller picture of their effect on the organism, the preparation of radioactive samples of the above compounds has a definite value. The radiocarbon, C^{14}, which is the most suitable isotope in this case for "labeling," has up to now been introduced into esters on the acid radical side. In 1955 Markova, Zenkova and Shchukina prepared paraminobenzoic acid, labeled with radioactive carbon in the carboxyl group and, using it, synthesized radioactive preparations of anesthesine and novocaine [1]. In 1956, we prepared the diphenylacetic ester of diethylaminoethanol (spasmolytin, transentine, diphacil), labeled with radioacarbon C^{14} in the carboxyl group of the diphenylacetic acid [2]. However, in order to have a complete biological study it is necessary to have a radioactive ester, labeled in the aminoalcohol radical. For this purpose we undertook to synthesize diethylaminoethanol, labeled with radiocarbon C^{14} in one of the ethyl groups.

Of the various practical methods of preparing diethylaminoethanol, we chose the synthesis that uses acetic acid as the starting radioactive material.

$$CH_3C^{14}OOH \xrightarrow{NH_3} CH_3C^{14}ONH_2 \rightarrow CH_3C^{14} \equiv N \xrightarrow{4H} CH_3C^{14}H_2NH_2 \xrightarrow{BrC_2H_5}$$

$$\rightarrow CH_3C^{14}H_2NHCH_2CH_3 \xrightarrow{ClCH_2CH_2OH} \begin{matrix} CH_3C^{14}H_2 \\ CH_3CH_2 \end{matrix} \!\!>\!\! NCH_2CH_2OH$$

EXPERIMENTAL

75 g of glacial acetic acid, mixed with radioactive acetic acid, $CH_3C^{14}OOH$, (total activity 10 mC), and excess ammonium carbonate, was heated in a flask connected to a short column, while it gently boiled for 1 hour. Then the temperature was increased and at 210-216° the acetamide distilled off and immediately solidified in the receiver. 35 g of acetamide, carefully mixed with 52 g of phosphorus pentoxide, was heated in a small Wurtz flask. Then the distillate was saturated with an equal volume of potassium carbonate and the acetonitrile distilled. B.p. 81-82°. 13 g of acetonitrile, prepared by the method described, was dissolved in 180 ml of anhydrous alcohol. The reduction was performed by adding metallic sodium to the solution. At the end of the reaction, the ethylamine was trapped with concentrated hydrochloric acid. The yield of ethylamine hydrochloride was 13 g. Then treatment of the ethylamine with excess ethyl bromide gave 6 g of diethylamine with b.p. 56-58°.

6 g of diethylamine and 6.5 g of ethylene chlorohydrin were heated in a flask with a reflux condenser on a water bath for 3 hours until the condensation of vapor and dripping of liquid ceased. On cooling, the reaction product set to a solid mass, to which was then added solid KOH. At the end of the reaction, the mass was extracted several times with ether. The extracts were dried with baked potassium carbonate and the ether distilled off on a water bath. The residue, diethylaminoethanol, was vacuum distilled. The product had b.p. 57-58° (14-15 mm). The yield was 6.5 g.

Found %: N 9.76. $C_8H_{15}ON$. Calculated %: N 9.93.

The radioactive yield was 5-6%, calculated on the starting active acid.

SUMMARY

We synthesized diethylaminoethanol labeled with radiocarbon C^{14} in one of the ethyl groups, which has not been described in the literature.

LITERATURE CITED

[1] Yu. V. Markova, L. N. Zenkova and M. N. Shchukina, J. Gen. Chem. 25, 1383 (1955).*

[2] L. B. Dashkevich, J. Gen. Chem. 27, 724 (1957).*

Received October 20, 1956

Leningrad Chemical Pharmaceutical Institute

* Original Russian pagination. See C. B. Translation.

THE INITIATING EFFECT OF SOME ACYL PEROXIDES

K. S. Minsker and L. V. Stupen

We previously [1] investigated the oxidizing effect of four acyl peroxides: acetylbenzoyl (ABP) and benzoyl (BP) peroxides and acetylated and benzoylated derivatives of hydroxycyclohexyl hydroperoxide (ACP) and (BCP), and put forward the hypothesis that the rate of the initiating effect is not related to the rate of the oxidizing effect; initiation is determined by the decomposition of peroxides to free radicals while the oxidizing effect proceeds by an ionic mechanism.

It seemed interesting to check our hypothesis and compare the effect of C_6H_5COO- and CH_3COO groups, of compounds of similar structure, (BP, and ABP, BCP and ACP) on their initiating activity in the block polymerization of vinyl chloride. ABP decomposes into two radicals: $C_6H_5CO_2 \cdot CH_3CO_2$. The effect of the latter may be seen by comparison with BP. The use of ABP as a polymerization initiator has been studied very little as yet [2].

BCP and ACP were tested only in styrene polymerization [3]. We determined the initiating effect of peroxides by the rate of peroxide accumulation in the initial period of vinyl chloride polymerization in the presence of air [4]. The method selected gave very consistent results.

The experiments were carried out in the presence of 0.03 mole of initiator with an equimolecular amount of peroxide oxygen. Vinyl chloride (3-5 g), containing the initiator, was poured into ampules (l = 150 mm, d = 28 mm), which were sealed and placed in a thermostat, at the experimental temperature, fitted with a special shaking device.

After a definite period of time the ampules were opened and the contents analyzed iodometrically.

The results of experiments at the two temperatures are given in the figure, which shows that the peroxide content increased during the reaction at a constant rate, regardless of the initiator used and that the substitution of an oxyacetyl by an oxybenzoyl group increased its activity during polymerization.

It should be noted that Cooper [3] gave almost equal rate constants for styrene polymerization with ACP and BCP, $1.91 \cdot 10^{-4}$ and $1.99 \cdot 10^{-4}$ mole $\cdot$ liter$^{-1} \cdot$ sec^{-1}, respectively.

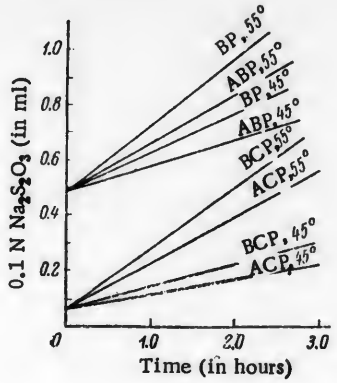
The relation found by us is in inverse proportion to the relative stability of the acetyloxy and benzoyloxy radicals [5].

As the initiating rate of peroxides is mainly determined by the relative rate of decomposition to free radicals, then, apparently, the presence of the CH_3CO_2 groups increases the stability of the $-O-O-$ bond in comparison with the peroxides containing $C_6H_5CO_2$ groups. This may be explained by some effective negative charge at the BP peroxide oxygen atoms, which facilitates decomposition [6].

From the results given in the figure, it is possible to characterize the relative stability of peroxides containing CH_3CO_2 groups in comparison with peroxides containing $C_6H_5CO_2$ groups, as 6.70 : 5 at 55° and 7.34 : 5 at 45°.

These values are close to the data on the relative stability of benzoyloxy and acetoyloxy radicals [5].

One can see by comparing the initiating effect of these peroxides with their oxidizing effect, that at 45° the peroxides may be arranged in the following series, according to the rate of their initiating action: BP > ABP



Initiating effect of benzoyl (BP) and acetylbenzoyl (ABP) peroxides and the benzoyl (BCP) and acetyl (ACP) derivatives of hydroxycyclohexyl hydroperoxide.

> BCP > ACP, which appears to coincide with the rate of the oxidizing action of these compounds. The only exceptions are BP and ABP, which liberate iodine completely in a few minutes.

But at 55° this relation breaks down: BP ≥ BCP > ABP ≥ ACP.

Thus, the hypothesis put forward earlier that no direct relation should exist between the oxidizing and initiating activities of peroxides has been confirmed.

It is our pleasant duty to thank Prof. G. A. Razuvaev for constant interest in the work and valuable advice.

SUMMARY

1. It was shown that the substitution of an oxyacetyl for an oxybenzoyl group increased the activity of a peroxide as an initiator of vinyl chloride polymerization in the presence of air.

2. The rate of acyl peroxide decomposition is in inverse proportion to the relative stability of the acyloxy radicals.

3. We confirmed the hypothesis that there is no relation between the initiating and oxidizing activity of acyl peroxides.

LITERATURE CITED

[1] G. A. Razuvaev, L. V. Stupen and K. S. Minsker, J. Gen. Chem. 26, 473 (1956).•

[2] I. Shaibler, Chemistry and Technology of Artificial Resins, •• State Chem. Press (1949).

[3] W. Cooper, J. Chem. Soc. 1951, 1340.

[4] K. S. Minsker, A. S. Shevlyakov and G. A. Razuvaev, J. Gen. Chem. 26, 1082 (1956).•

[5] G. A. Razuvaev, Yu. A. Oldekop and V. N. Latyaeva, J. Gen. Chem. 26, 1110 (1956).•

[6] R. I. Milyutinskaya and Kh. S. Bagdasaryan, J. Phys. Chem. 28, 797 (1954).

Received October 20, 1956

• Original Russian pagination. See C. B. Translation.
•• In Russian.

THE THERMOCHEMISTRY OF SUBSTITUTION IN THE AROMATIC NUCLEUS

I. THE HEAT EFFECT IN THE SULFONATION OF RESORCINOL

V. N. Kiselnikov and T. S. Kazas

Up to the present time the heat effects in the sulfonation of organic compounds and the heats of combustion and formation of sulfonic acids have been determined experimentally only in a very limited number of cases.

A. A. Spryskov [1] found that the heat of sulfonation in liquid naphthalene was about 5 kcal/mole. Experimental determination of the heat effect of sulfonation is rather difficult as at high temperatures this reaction often proceeds nonquantitatively with the formation of various side products.

The heats of combustion of sulfonic acids have been determined only for the trihydrate of β-naphthalene sulfonic acid, p-toluene sulfonic acid and of 2,4-dinitro-1-naphthol-7-sulfonic acid [2] and are difficult to use for calculating the heat effect of sulfonation and the heats of formation of sulfonic acids. Luginin [3] mentions the considerable difficulty in determining experimentally the heats of combustion of organic sulfonic acids due to their infusibility, involatility and obscure sulfur oxidation processes. It should be noted that reliable results cannot be achieved by calculating the heat effect of sulfonation from the heats of combustion of sulfonic acids. Small relative errors in determining the heats of combustion and formation of compounds led to large errors in determining the heat effect of sulfonation as the latter is the difference between the heats of formation of reaction products and the reacting substances and its absolute value is very small.

In technological calculations of sulfonation processes, it is usual to use the heat of combustion of compounds determined by the empirical formulas of Sventoslavsky [4], Kharasch [5] and others. However, these formulas do not give accurate results in calculating the heat effects of sulfonation and substitution of sulfonic groups. Therefore, it seemed interesting to determine experimentally the heat effects of sulfonation of those compounds which are sulfonated quantitatively even at temperatures suitable for calorimetry. According to us, such a compound is resorcinol.

As is known, resorcinol is readily sulfonated to the disulfonic acid at room temperature in excess concentrated sulfuric acid. In order to prove the formation of the disulfonic acid, Fischer [6] prepared its barium and potassium salts with the following compositions: $C_6H_2(OH)_2(SO_3)_2Ba \cdot 3H_2O$ and $C_6H_2(OH)_2(SO_3)_2K_2 \cdot H_2O$. We decided to use this reaction to determine the heat effect of sulfonation and for this purpose we investigated resorcinol sulfonation at temperatures of 15, 20, 25 and 100° with concentrated (93.5 and 94.77%) sulfuric acid.

EXPERIMENTAL

Sulfonation of resorcinol. For analysis of the sulfonic mass obtained the following method was used.

We determined the total acidity of the sulfonic mass and the free sulfuric acid by precipitating it with barium chloride solution. By a special experiment on an artificial mixture of sulfuric acid and the potassium salt of resorcinol disulfonic acid we proved that under these conditions only sulfuric acid was precipitated.

Resorcinol disulfonic acid was determined as the barium salt. For this purpose a separate sample of the sulfonic mass was neutralized with barium carbonate and this first precipitated barium sulfate. The precipitate of barium sulfate obtained was filtered off from the solution of barium resorcinol disulfonate. The completeness of the separation was checked by the color with ferric chloride (in the presence of resorcinol disulfonic acid,

TABLE 1

Results of Experiments on the Sulfonation of Resorcinol

Experiment No.	Temperature	Used for the experiment (in g)			Resorcinol disulfonic acid expected by calculation (g)	Determined (g)		
		Resorcinol	Sulfuric acid, calculated on 100%	Ratio (in moles)		Resorcinol disulfonic acid		free resorcinol
						as the barium salt	by analysis of the acidity of the sulfonic mass	
1	15°	2.00	26.70	1 : 15	4.91	4.74	4.82	0.0545
2	20	4.24	55.51	1 : 14.7	10.41	10.20	10.20	absent
3	20	3.90	47.28	1 : 13.6	9.57	10.21	9.25	
4	20	3.81	50.30	1 : 14.8	9.35	9.74	8.60	
5	25	3.00	37.96	1 : 15	7.36	8.63	7.90	
6	25	3.00	37.96	1 : 15	7.36	7.38	8.19	
7	25	3.00	37.96	1 : 15	7.36	8.23	7.85	
8	25	3.00	37.96	1 : 15	7.36	8.96	7.51	
9	100	4.035	37.77	1 : 10.5	9.90	—	9.60	
10	100	3.14	54.09	1 : 19.5	7.70	—	7.50	
11	100	3.20	53.47	1 : 18.8	7.85	—	8.00	

ferric chloride gives a violet color). Then, on evaporation, the filtrate gave barium resorcinol disulfonate. The resorcinol monosulfonic acid remained in the solution, from which it was isolated in the form of the lead salt by treating the solution with lead acetate. The residue of unsulfonated resorcinol was determined by bromination with bromide-bromate.

The results of our experiments on the sulfonation of resorcinol are given in Table 1.

In order to obtain additional evidence on the formation of the disulfonic acid in the sulfonation of resorcinol, we carried out an analysis on the barium disulfonate obtained and on the potassium salt prepared from it.

Analysis of barium salt. 1.2502, 1.0020 g of material: 0.6346, 0.5004 g of $BaSO_4$. 1.3562 g of material: 0.1594 g of H_2O (dried at 130°). Found %: Ba 29.87, 29.37; H_2O 11.75. $C_6H_4O_8S_2Ba \cdot 3H_2O$. Calculated %: Ba 29.88; H_2O 11.76.

Analysis of potassium salt. 0.7260 g of material: 0.3500 g of K_2SO_4. 4.212 g of material: 0.1972 g of H_2O. Found %: K 21.63; H_2O 4.68. $C_6H_4O_8S_2K_2 \cdot H_2O$. Calculated %: K 21.46; H_2O 4.94.

Thus, from our experiments on the sulfonation of resorcinol, we may come to the following main conclusions.

1. On sulfonating resorcinol at 20, 25 and 100° in excess concentrated sulfuric acid, it is quantitatively converted into the disulfonic acid.

2. At 15°, about 2.7% of the resorcinol remains unsulfonated.

3. We were not able to isolate resorcinol monosulfonic acid from the sulfonic mass in sufficient amounts for analysis.

4. Analysis of the barium and potassium salts of resorcinol disulfonic acid isolated confirmed the formulas of Fischer [6].

The heat effect of the sulfonation of resorcinol. We carried out two series of experiments on the determination of the heat effect in the sulfonation of resorcinol.

The first series of experiments was carried out in a calorimeter, which consisted of a glass vessel with vacuum walls (Dewar vessel), which was placed in a thermostat, fitted with a temperature regulator. In the calorimeter was a stirrer and a Beckmann thermometer. Before the experiment the constant of the calorimeter was determined, then sulfuric acid was loaded into the calorimeter, followed by a glass ampoule with a determined weight of resorcinol. The experiment was begun when a constant temperature was established in the

TABLE 2

Heat Effect of Resorcinol Sulfonation in a Homogeneous Medium (first series of experiments)

Experiment No.	Used for the experiment: resorcinol (g)	sulfuric acid: (g)	sulfuric acid: % content	Observed temperature rise	Correction to Δt	Δt	Length of main period (in minutes)	Heat equivalent of calorimeter (in cal/deg)	Heat capacity of sulfonation mixture (in cal/g · deg)	Observed heat effect −ΔH (kcal/mole)	Heat effect −ΔH (kcal/mole): dilution of sulfuric acid	Heat effect −ΔH (kcal/mole): sulfonation
1	2.5000	363.98	93.59	2.955°	—0.076°	2.879°	129	24.50	0.372	20.40	14.36	6.06
2	7.1559	1168.70	93.59	2.770	—0.0375	2.7325	150	36.41	0.372	19.92	14.27	5.65
3	6.6608	1154.71	93.50	2.454	+0.0158	2.4698	180	36.41	0.388	19.91	14.22	5.69
4	6.2816	1160.74	93.59	2.476	—0.010	2.466	180	36.41	0.367	20.29	14.28	6.01
									Average value of heat effect in sulfonation of resorcinol − H kcal/mole			5.85±0.2

TABLE 3

Heat Effect of Resorcinol Sulfonation in a Heterogeneous Medium (first series of experiments)
Heat equivalent of calorimeter 36.4 kcal/deg.

Experiment No.	Used for the experiment: resorcinol (g)	sulfuric acid: (g)	sulfuric acid: % content	Observed temperature rise	Correction to Δt	Δt	Length of main period (in minutes)	Heat capacity of sulfonation mixture (in cal/g · deg)	Observed heat effect −ΔH (kcal/mole)	Heat effect: dilution of sulfuric acid	Heat effect: sulfonation
1	5.6460	1125.66	89.25	2.092°	—0.100°	1.992°	180	0.3571	17.10	12.58	5.44
2	3.6425	1113.12	88.10	1.445	—0.092	1.353	210	0.3615	18.07	12.00	6.07
3	6.0019	1123.98	92.85	2.327	—0.2291	2.0279	190	0.3883	17.72	14.16	3.56
4	6.7575	1106.74	90.25	2.734	—0.2075	2.5265	150	0.365	18.23	13.64	4.59
5	5.4163	1121.96	90.0	2.068	—0.095	1.973	180	0.3662	18.00	12.86	5.04
6	4.873	1090.52	89.25	1.970	—0.036	1.934	180	0.346	18.13	12.58	5.55
									Average value		5.0±1.0

TABLE 4

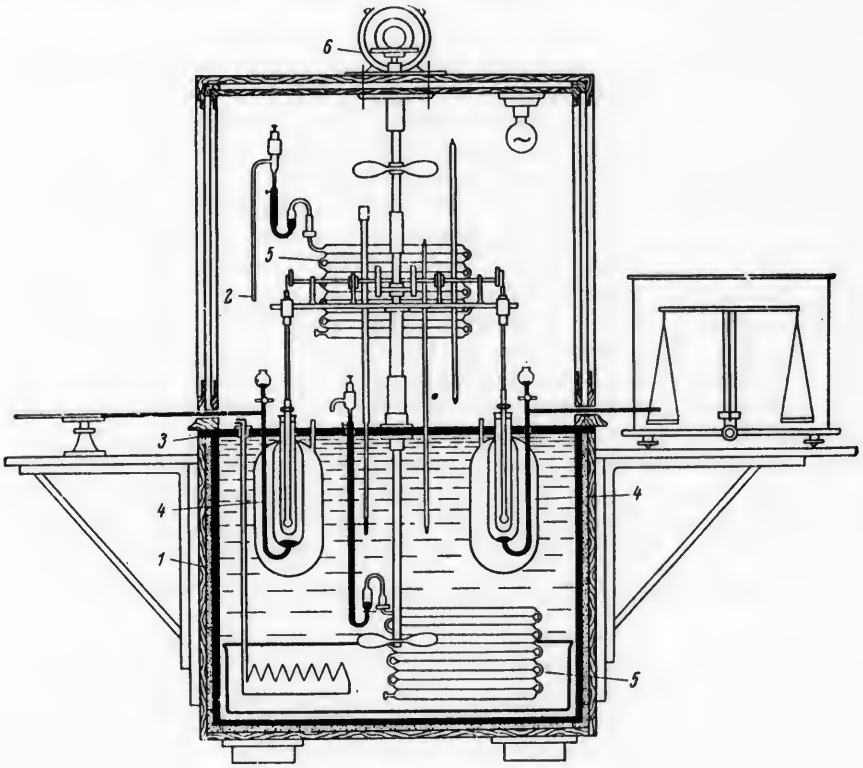
Heat Effect of Resorcinol Sulfonation in a Homogeneous Medium (second series of experiments)

0.5 g of resorcinol and 73.4 g of 93.5% sulfuric acid were used

Experiment No.	Observed mercury movement in capillary (in mm)*	Correction for radiation (in mm)	Length of main period (in min)	Observed heat effect $-\Delta H$ (kcal/mole)	Heat effect of resorcinol sulfonation** $-\Delta H$ (kcal/mole)
1	502.5	—30.0	90	20.60	6.32
2	481.0	—27.3	105	19.73	5.45
3	471.0	—53.0	102	18.28	4.00
4	517.5	—64.8	90	19.27	4.99
5	488.0	—46.8	90	19.30	5.02
			Average value		5.2±1.1

* The value of 1 mm movement of mercury was 0.198 cal.

** The heat effect of the dilution of H_2SO_4 is 14.28 kcal/mole.



Plan of calorimetric apparatus.
Explanation in text.

calorimeter. After the experiment, the heat capacity of the mass was determined. All the experiments on the heat effects in the first series were carried out with an initial temperature of 20°.

We determined the heat effects in the sulfonation of resorcinol both under conditions of complete solution of the resorcinol and the sulfonation products in sulfuric acid, using a large excess of sulfuric acid, i.e., in a homogeneous medium, and under conditions of separation of the sulfonation products from the solution, i.e., in a heterogeneous medium. In the latter case the sulfonation of resorcinol was carried out with a comparatively small excess of sulfuric acid or we sulfonated separate portions of resorcinol successively several times in the same sulfonation mixture. In the latter sulfonations of resorcinol, its disulfonic acid precipitated completely from the solution.

By these experiments, we established that the solubility of resorcinol disulfonic acid in 93% sulfuric acid is about 1.5%. The results of the experiments on the heat effects in the sulfonation of resorcinol are given in Tables 2 and 3.

The correction to the observed temperature difference was calculated by the Renier-Pfaundler formula [7]. The heat effect of dilution of the sulfuric acid was calculated from Brönsted's data [8]; however, determination of the heat effects in the sulfonation of resorcinol by this method was made difficult by the determination of the radiation heat loss during the long sulfonation process and also the additional determination of the heat capacity of the sulfonation mixture.

The second series of experiments was performed in an isothermal calorimeter, in which we usually used diphenyl oxide as the working material. For rapidity of measurement, we usedthe apparatus with two calorimeters, illustrated in the figure.

The calorimetric apparatus consisted of a water thermostat 1 and an air thermostat 2, fitted with double glass walls, from which the front wall slid out. The volume of each thermostat was about 100 liters. Into the plastic cover 3 of the water thermostat were fixed two diphenyl oxide calorimeters 4 with the working volume of the reaction tube equal to about 40 ml. For convenience in measuring considerable heat effects, the reaction capillary of the right calorimeter was connected to scales for weighing the mercury discharged from the calorimeter when the diphenyl oxide melted during exothermic reactions. The measurement of small or negative heat effects was carried out in the left calorimeter using the movement of the mercury in the capillary. The water and air thermostats were fitted with metal toluene thermoregulators 5 with a surface of 1700 cm^2 and a volume of 700 ml, which allowed temperature regulation with an accuracy of 0.002°. The temperature of the thermostat was measured with a Beckmann thermometer. The thermostats were heated with electric heaters, connected to a relay and an autotransformer. The thermostat was fitted with a propeller stirrer, driven by a motor through a friction transmission 6. The reaction mixture in the calorimeter was mixed either with a propeller stirrer or a rocking mixer, which derived its reciprocating motion from the same motor. The calorimeters were calibrated before the experiments. By dissolving a determined sample of the dry salts lithium chloride or potassium chloride in the calorimeter, we determined the value of one graduation of movement of the mercury in the capillary and the value of one gram of mercury expelled, in calories. In addition, we also carried out this calibration using a resistance spiral, through which a definite amount of electric current was passed. In all cases, the temperature of the experiment equalled the melting point of diphenyl oxide, i.e., 26.75°.

The heat effects in the sulfonation of resorcinol, which we determined by this method, are given in Tables 4 and 5.

From a comparison of the values of the heat effects in the sulfonation of resorcinol, which we obtained by the two different methods, it appears that there is a difference in the value of the sulfonation heat effect, determined in a homogeneous medium and under conditions where the resorcinol disulfonic acid formed precipitated. In the first series of experiments, this difference was 0.85 kcal/mole and in the second, 1.6 kcal/mole. This difference is the heat effect in the crystallization of resorcinol disulfonic acid. It is probable that in the second series of experiments the crystallization of resorcinol disulfonic acid during the sulfonation occurs more completely as here a considerable amount of resorcinol disulfonic acid was added to the sulfonating acid before the sulfonation process and, in addition, the concentration of the sulfonating acid was somewhat higher and constant. Therefore, as it seemed to us, preference should be given to the results obtained in the second series of experiments.

In our experiments on the determination of the heat effects in resorcinol sulfonation, solid resorcinol was added to the sulfonating sulfuric acid. Thus, the heat of solution of resorcinol is included in the sulfonation heat effect, determined by us.

We carried out special experiments to determine the heat effect in the solution of resorcinol in alkali.

$m\text{-}C_6H_4(OH)_{2(solid)} + 2NaOH_{(dissolved)} = m\text{-}C_6H_4(ONa)_{2(dissolved)} + 2H_2O$; $\Delta H = -14.3$ kcal/mole .

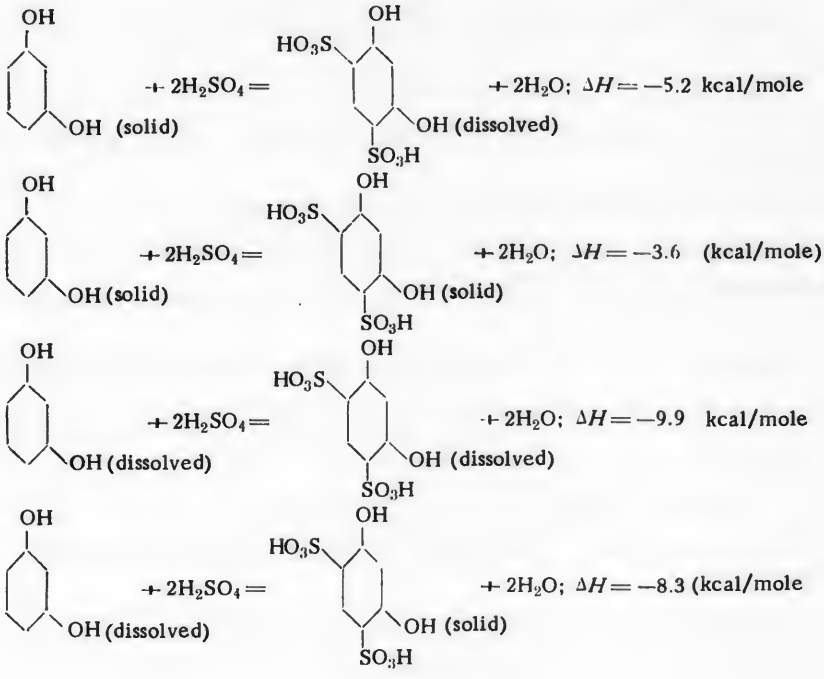
$m\text{-}C_6H_4(OH)_{2(dissolved)} + 2NaOH_{(dissolved)} = m\text{-}C_6H_4(ONa)_{2(dissolved)} + 2H_2O$; $\Delta H = -19.0$ kcal/mole.

Hence:

$m\text{-}C_6H_4(OH)_{2(solid)} \rightarrow m\text{-}C_6H_4(OH)_{2(dissolved)}$; $\Delta H = 4.7$ kcal/mole.

We should note that the heat effect in the solution of resorcinol, which we determined, is close to its heat of fusion.

The heat of fusion of resorcinol (given in the Chemist's Handbook, vol. III) is 5.09 kcal/mole. Thus, allowing for the heat of solution of resorcinol, we may calculate the heat effect in sulfonating it to the disulfonic acid derivative:



The latter value is close to the heat effect of the sulfonation of liquid naphthalene to the monosulfonic acid [1].

TABLE 5

Heat Effect of Resorcinol Sulfonation in a Heterogeneous Medium
(second series of experiments)
0.5 g of resorcinol, 3.0 g of disulfonic acid and 73.4 g of 93.5% sulfuric acid were used

Experiment No.	Observed mercury movement in capillary (in mm)*	Corrosion for radiation (in mm)	Length of main period (in min)	Observed heat effect $-\Delta H$ (kcal/mole)	Heat effect of resorcinol sulfonation** $-\Delta H$ (kcal/mole)
1	450	—40.8	90	17.83	3.55
2	476	—72	90	17.61	3.33
3	487	—72	90	18.09	3.81
4	471	—81	90	17.01	2.73
5	495	—66	100	18.71	4.43
			Average value		3.6±1.1

* The value of 1 mm movement of mercury was 0.198 cal.
** The heat effect of the dilution of H_2SO_4 is 14.28 kcal/mole.

SUMMARY

1. Resorcinol was quantitatively converted into resorcinol disulfonic acid by sulfonation in excess concentrated sulfuric acid.

2. The heat effect of solid resorcinol sulfonation equals 5.2 kcal/mole.

3. The heat effect of dissolved resorcinol sulfonation equals 9.9 kcal/mole.

4. We determined the heat of crystallization of resorcinol disulfonic acid in concentrated (93%) sulfuric acid, which is 1.6 kcal/mole.

5. The solubility of resorcinol disulfonic acid in concentrated (93%) sulfuric acid is about 1.5%.

LITERATURE CITED

[1] A. A. Spryskov, J. Gen. Chem. 18, 99 (1948).

[2] L.-B. T., II Ergbd., 1651 (1931).

[3] V. F. Luginin, Description of Various Methods for Determining the Heats of Combustion of Organic Compounds*, Moscow (1894).

[4] V. V. Sventoslavsky, J. Russ. Phys. Chem. Soc. 9, 1257, 1602 (1908).

[5] M. S. Kharasch, Journ. Res. NBS, 2, 359 (1929).

[6] H. Fischer, Monatsh. 2, 331 (1881).

[7] M. M. Popov, Thermometry and Calorimetry*, II Edit., 394 (1954).

[8] I. N. Brönsted, Z. phys. Chm. 68, 693 (1910).

Received September 10, 1956

Ivanov Chemical Technology Institute

* In Russian.

SYNTHESIS USING ACRYLONITRILE

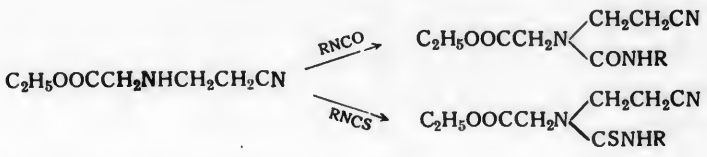
XXXII. SOME DERIVATIVES OF CYANOETHYLATED α-AMINO ACIDS

A. P. Terentyev and P. F. Butskus

In previous papers we described methods of preparing N-cyanoethylated α-amino acids [1], their esters and amides [2] and cyanoethylated diketopiperazines and glycylglycine [1, 3]. Surmising that the derivatives of cyanoethylated amino acids are of interest and may be widely used in organic synthesis, in this paper we continue the report on our investigations in this field.

Using one of the above methods [2], we cyanoethylated the ethyl ester of alanine. Treatment of the cyanoethylation product with an alcohol ammonia solution gave N-cyanoethyl-alanine amide.

Treatment of the ethyl ester of N-cyanoethyl-glycine with phenyl isocyanate, α-naphthyl isocyanate or phenyl isothiocyanate gave, in almost quantitative yield, addition products by the scheme

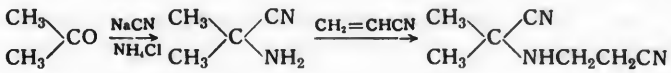


The esters of N, N-dicyanoethyl-glycine gave no addition products with isocyanates and isothiocyanates.

The esters of cyanoethylated amino acids reacted with hydrazine hydrate in the cold with the evolution of heat. This gave hydrazides of N-cyanoethylated α-amino acids.

$$C_2H_5OOCCH(R)NHCH_2CH_2CN + NH_2NH_2 \rightarrow$$
$$\rightarrow H_2NNHCOCH(R)NHCH_2CH_2CN + C_2H_5OH$$
$$R = H,\ CH_3,\ C_6H_5CH_2$$

The cyanoethylation of amino acid nitriles was studied using as an example α-aminoisobutyronitrile. The latter was prepared by Zelinsky and Stadnikov's method [4] and was treated with acrylonitrile without being isolated from the reaction mixture. N-Cyanoethyl-α-aminoisobutyronitrile was isolated. The reaction proceeded by the scheme



As a side product of this reaction, the cyanoethylation product of hydrocyanic acid, succinodinitrile, was isolated which when hydrolyzed and then esterified gave diethyl succinate.

There are several examples known in the literature where certain amines were used instead of ammonia in the synthesis of α-aminonitriles by Strecker's method and amine hydrochlorides were used, instead of ammonium

chloride, by Zelinsky and Stadnikov's method. We assumed that the ammonium chloride in the Zelinsky and Stadnikov reaction could be substituted by β-aminopropionitrile hydrochloride (monocyanoethylated ammonia). Under these conditions we would expect the formation of the corresponding N-monocyanoethylated α-aminonitrile. In fact, treatment of acetone with sodium cyanide and β-aminonitrile hydrochloride gave N-cyanoethyl-α-amino-isobutyronitrile, whose constants agreed with the monocyanoethylation product of α-aminoisobutyronitrile.

EXPERIMENTAL

1. The ethyl ester of N-cyanoethyl-alanine. The reaction was carried out by the method described previously (see [2]; experiment 1-b). 5 ml of water, 6.9 g of acrylonitrile and 3.7 g of potassium hydroxide, dissolved in 15 ml of water, were added to 10 g of the ethyl ester of alanine hydrochloride. The mixture was heated for 4-5 hours at 65-70°. The yield of the ethyl ester of N-cyanoethyl-alanine was 7.5 g (68%). The b.p. was 157-158° at 20 mm; it was a colorless liquid, dissolving in water, alcohol and ether.

d_4^{20} 1.0209, n_D^{20} 1.4435, MR_D 44.24; calc. 44.22.
Found %: C 56.48, 56.37; H 8.29, 8.42; N 16.37, 16.48. $C_6H_{14}O_2N_2$. Calculated %: C 56.44; H 8.29; N 16.45.

The hydrochloride had m. p. 174° (from alcohol). It was readily soluble in water and boiling alcohol.

Found %: Cl 17.03, 16.96. $C_6H_{15}O_2N_2Cl$. Calculated %: Cl 17.15.

2. The amide of N-cyanoethyl-alanine. 3 g of the ethyl ester of N-cyanoethyl-alanine was treated for 2 days with 80 ml of an alcohol solution of ammonia. The yield of amide was 1.9 g (76%). The m. p. was 80.5-81.5° (from alcohol). The material was soluble in water and alcohol.

Found %: N 29.72, 29.61. $C_6H_{11}ON_3$. Calculated %: N 29.76.

3. The ethyl ester of N-cyanoethyl-ω-phenylureidoacetic acid. 1.5 g of phenyl isocyanate was gradually added with stirring to a solution of 2 g of the ethyl ester of N-cyanoethyl-glycine in 30 ml of anhydrous ether. After standing for 1 hour, the precipitate of the ethyl ester of N-cyanoethyl-ω-phenylureidoacetic acid was filtered off and washed with ether. The yield was 3.4 g (97.1%). On recrystallization from water, we obtained plate-like crystals with m. p. 123°, which were difficultly soluble in cold water, more readily in hot, readily soluble in alcohol and insoluble in ether.

Found %: C 61.23, 61.06; H 6.34, 6.27; N 15.13, 15.05. $C_{14}H_{17}O_3N_3$. Calculated %: C 61.07; H 6.22; N 15.26.

4. The ethyl ester of N-cyanoethyl-ω-(α-naphthyl)-ureidoacetic acid. 2.2 g of α-naphthyl isocyanate was added to a solution of 0.2 g of ethyl ester of N-cyanoethyl-glycine in 30 ml of anhydrous ether. The reaction was carried out as in experiment 3. The ethyl ester of N-cyanoethyl-ω-(α-naphthyl)-ureidoacetic acid was an amorphous substance with m.p. 99° (from benzene). The yield was 4.4 g (97.6%). The substance was soluble in hot benzene, very difficultly soluble in hot water and insoluble in cold water, alcohol and ether.

Found %: C 66.64, 66.64; H 6.22, 6.32; N 12.64, 12.81. $C_{18}H_{19}O_3N_3$. Calculated %: C 66.44; H 5.88; N 12.91.

5. The ethyl ester of N-cyanoethyl-ω-phenylthioureidoacetic acid. 1.7 g of phenyl isothiocyanate was added to a solution of 2 g of the ethyl ester of N-cyanoethyl-glycine in 30 ml of anhydrous ether. The reaction was carried out as in experiment 3. The yield of the ethyl ester of N-cyanoethyl-ω-phenylthioureidoacetic acid was 3.6 g (97.3%). The m.p. was 184°. The material was very difficultly soluble on heating in alcohol and benzene and insoluble in ether and cold water.

Found %: C 57.90, 57.81; H 5.83, 5.92; N 14.16, 14.30. $C_{14}H_{17}O_2N_3S$. Calculated %: C 57.71; H 5.88; N 14.42.

6. N-Cyanoethyl-glycine hydrazide. 14 g of the ethyl ester of N-cyanoethyl-glycine was gradually added with cooling and stirring to 5.5 g of hydrazine hydrate. The mixture was left to stand overnight at room temperature. The excess hydrazine hydrate and the ethyl alcohol formed were distilled off in vacuum, the reaction product was washed 4-5 times with small amounts of anhydrous ether and the remains of the latter were also removed in vacuum. The N-cyanoethylglycine hydrazide, which was obtained as a clear, colorless oil, crystallized

on cooling. The yield was 11.6 g (91.3%). The m.p. was 69° (from alcohol). The material was readily soluble in water and hot alcohol, soluble in ethyl acetate, chloroform and dioxane and insoluble in ether. On heating, it reduced an ammonia solution of silver oxide and Fehling's solution.

Found %: C 42.29, 42.41; H 7.18, 7.19; N 39.06, 38.99. $C_5H_{10}ON_4$. Calculated %: C 42.24; H 7.09; N 39.41.

7. N-Cyanoethyl-alanine hydrazide. 2.5 g of the ethyl ester of N-cyanoethyl-alanine was added to 0.8 g of hydrazine hydrate. The reaction and isolation of the product were carried out as in experiment 6. The N-cyanoethyl-alanine hydrazide, which was obtained as a clear, colorless oil, crystallized on cooling. The yield was 1.9 g (82.6%). The m. p. was 97.5° (from alcohol). The material was readily soluble in water and hot alcohol and insoluble in ether.

Found %: C 46.12, 46.27; H 7.82, 7.82. $C_6H_{12}ON_4$. Calculated %: C 46.13; H 7.74.

8. N-Cyanoethyl-β-phenylalanine hydrazide. A mixture of 2.5 g of the ethyl ester of N-cyanoethyl-phenylalanine and 0.6 g of hydrazine hydrate was shaken for 2 hours and left to stand overnight. The solid mass was separated from the liquid and washed with small amounts of cold alcohol and anhydrous ether. The yield of N-cyanoethyl-β-phenylalanine hydrazide was 2 g (87%). On recrystallization from alcohol, it formed plate-like crystals with m.p. 120.5-121°. It was readily soluble in water and hot alcohol and insoluble in ether.

Found %: C 62.54, 62.31; H 7.22, 7.20; N 23.94, 24.67. $C_{12}H_{16}ON_4$. Calculated %: C 62.04; H 6.94; N 24.12.

9. N-Cyanoethyl-α-aminoisobutyronitrile. a) α-Aminoisobutyronitrile was prepared by Zelinsky and Stadnikov's method [4] from equimolecular amounts of sodium cyanide (33.8 g), ammonium chloride (36.8 g) and acetone (40 g). Without isolating the α-aminoisobutyronitrile, the reaction mixture was placed in a three-necked, round-bottomed flask, fitted with a mechanical stirrer, dropping funnel and a reflux condenser. A solution of 2-3 g of sodium hydroxide in 10 ml of water was added to the mixture and in 1 hour, 29 g of acrylonitrile was run in with stirring. After 4 hours stirring and standing for 8-10 hours, the mixture was heated at 70-75° for 1 hour. The oily reaction product was separated from the aqueous layer; the latter was extracted 3-4 times with ether. The ether extracts were combined with the upper layer and dried with sodium sulfate. The ether was distilled and the residue vacuum distilled. At 58-59° and 15 mm, 1-2 g of unreacted α-aminoisobutyronitrile (hydrochloride with m.p. 143-145°; literature data: m. p. 144-146° [5]) distilled over. The boiling point of the N-cyanoethyl-α-aminoisobutyronitrile was 115-116° at 15 mm. The yield was 32 g (40%, calculated on the acrylonitrile). At 149-151° (15 mm) 3-6 g of succinodinitrile distilled over. The latter solidified at 51-52°. Literature data: b. p. 158-160° at 20 mm; solidification temperature, 53° [6].

Found %: C 59.82, 59.91; H 5.18, 5.21. $C_4H_4N_2$. Calculated %: C 59.98; H 5.03.

On heating the reaction mixture longer, the yield of succinodinitrile increased. In the reaction flask was left a considerable amount of undistillable tarry material.

On hydrolyzing the succinodinitrile with hydrochloric acid and subsequently esterifying, we obtained the diethyl ester of succinic acid in 60% yield.

B. p. 104-105° at 15 mm, which corresponds to the literature data [7]: n_D^{20} 1.4210, d_4^{20} 1.0402; MR_D 42.46; calc. 42.45

Found %: C 55.35, 55.15; H 8.25, 8.09. $C_8H_{14}O_4$. Calculated %: C 55.16; H 8.10.

b) 12.6 g of sodium cyanide and 27.5 g of β-aminopropionitrile hydrochloride were dissolved in 80 ml of water in a thick-walled bottle. 15 g of acetone was added to the solution, which was shaken for 10 hours. The mixture was left over night and then heated for 7 hours at 50-60°. Further treatment was as in experiment 9a. The yield of N-cyanoethyl-α-aminoisobutyronitrile was 23.5 g (66.4%). The b. p. was 115-116° (15 mm). The colorless liquid was readily soluble in water and ether and had a characteristic nitrile smell.

n_D^{20} 1.4505, d_4^{20} 0.9684, MR_D 37.90; calc. 37.76.
Found %: C 61.23, 61.23; H 8.26, 8.30; N 30.39, 30.37. $C_7H_{11}N_3$. Calculated %: C 61.28; H 8.08; N 30.63.

The hydrochloride had m. p. 165.5° (from alcohol). It was readily soluble in water and boiling alcohol.

Found %: N 23.94, 24.05. $C_7H_{12}N_3Cl$. Calculated %: N 24.20.

SUMMARY

We prepared the ethyl ester and the amide of N-cyanoethyl-alanine and the products of isocyanate and isothiocyanate addition to the ethyl ester of N-cyanoethyl-glycine.

When treated with hydrazine hydrate the esters of cyanoethylated α-amino acids gave hydrazides of cyanoethylated α-amino acids. The hydrazides of N-cyanoethylated glycine, alanine and phenylalanine were prepared.

We showed the possibility of substituting the ammonium chloride in the Zelinsky and Stadnikov reaction by β-aminopropionitrile hydrochloride in the synthesis of N-monocyanoethylated α-amino acid nitriles. We prepared N-cyanoethyl-α-aminoisobutyronitrile and its hydrochloride.

LITERATURE CITED

[1] A. P. Terentyev, P. F. Butskus, J. Gen. Chem. 27, 2591 (1957).*

[2] A. P. Terentyev, P. F. Butskus, J. Gen. Chem. 23, 1230 (1953).*

[3] A. P. Terentyev, P. F. Butskus, Proc. Acad. Sci. USSR, 97, 851 (1954).

[4] N. D. Zelinsky, G. L. Stadnikov, J. Russ. Chem. Soc. 38, 722 (1906).

[5] W. Gulewitsch, T. Wasmus, Ber. 39, 1187 (1906).

[6] Beilst, 2, 615.

[7] Beilst, 2, 609.

Received October 20, 1956

Moscow State University and
Vilna State University

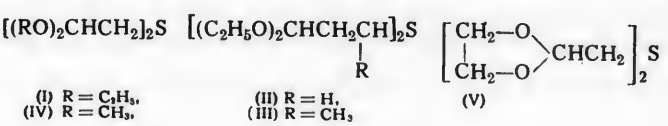
* Original Russian pagination. See C. B. Translation.

SYNTHESIS OF SOME THIODIALDEHYDE ACETALS

S. M. Gurvich

It is known that α,α,ω-trialkoxy- and α,α,ω,ω-tetraalkoxyalkanes with not less than 3 carbon atoms in the main chain are effective foaming agents in the flotation of nonferrous metal ores[1]. In connection with this, it seemed interesting to study the foaming effect of those analogs of the above compounds which have the central methylene group substituted by a sulfur atom.

For this purpose we synthesized a series of symmetrical thiodialdehyde acetals, among them: the diethylacetals of thiodiacetaldehyde (I), thio-β,β'-dipropionaldehyde (II) and thio-β,β'-dibutyraldehyde (III), and the dimethylacetal (IV) and ethylene dihydroxyacetal (V) of thiodiacetaldehyde.



(I) R = C_2H_5, (IV) R = CH_3. (II) R = H, (III) R = CH_3 (V)

All the thiodialdehyde acetals were prepared by heating the corresponding monohaloaldehyde acetals with sodium sulfide in an aqueous alcohol solution.

Bromoacetaldehyde diethylacetal was synthesized by treating a solution of vinyl acetate with bromine in anhydrous alcohol; the dimethyl- and ethylene dihydroxyacetals of bromoacetaldehyde were prepared analogously by substituting the anhydrous alcohol by anhydrous methyl alcohol and ethylene glycol, respectively. The diethylacetals of β-chloropropionaldehyde and β-chlorobutyraldehyde were prepared by treating acrolein and crotonaldehyde with a solution of dry hydrogen chloride in anhydrous alcohol.

Laboratory flotation tests of the thiodialdehyde acetals synthesized [2] showed that some of them are very valuable foaming agents both in foaming capacity and in selectivity of action in the flotation of polymetallic ores [3]. The preparations studied may be arranged according to their foaming value in the following order (I), (IV), (V), (II), (III), with the latter two considerably surpassed by the first three and thus not worth considering as possibilities.

The author expresses his thanks to A. K. Livshits for proposing the theme and to S. V. Didenkov for the flotation tests.

EXPERIMENTAL*

The diethylacetal of bromoacetaldehyde was prepared by the method of [4]; the yield was 51% and the b.p. 62-63° at 15 mm.

Diethylacetal of thiodiacetaldehyde (I). A solution of 15 g of $Na_2S \cdot 9H_2O$ in 100 ml of alcohol and 15 g of the diethylacetal of bromoacetaldehyde were heated in a steel ampule for 3 hours at 160°; the alcohol was distilled off from the cooled reaction mixture in vacuum, the residue diluted with two volumes of water, the separated aqueous layer extracted with ether (4 times with 30 ml each), the ether extract combined with the organic layer and dried with K_2CO_3 and the (I) isolated. The yield was 6.8 g (67%).

* Carried out with the participation of R. Ya. Belova.

B. p. 131° at 5 mm, 126° at 4 mm, d_4^{20} 0.9876, n_D^{20} 1.4495. Literature data: b.p. 143-147° at 11 mm [5], 147-148° at 12 mm, $d^{23.5}$ 0.9863, n_D^{23} 1.4473 [6].

The diethylacetal of β-chloropropionaldehyde was prepared by the method in [7]; the yield was 28%, the b.p. 58-62° at 8 mm, d_4^{20} 0.9733, n_D^{20} 1.4189.

The diethylacetal of thio-β-β'-dipropionaldehyde (II), was prepared similarly to (I) from 10 g of the diethylacetal of β-chloropropionaldehyde and 10 g of $Na_2S \cdot 9H_2O$ in 65 ml of alcohol (160°, 3 hours) and the yield was 4.5 g (60%).

B. p. 152-154° at 4 mm, d_4^{20} 0.9785, n_D^{20} 1.4511, MR_D 81.04; calc. 81.39.
Found %: S 11.25, 11.22. $C_{14}H_{30}O_4S$. Calculated %: S 10.89.

The diethylacetal of β-chlorobutyraldehyde was prepared from 35 g of crotonaldehyde and 75 ml of anhydrous alcohol, saturated with hydrogen chloride; the yield was 18 g (20%).

B. p. 69-71° at 11 mm, d_4^{20} 0.9719, n_D^{20} 1.4189, MR_D 46.89; calc. 47.30. Literature data [8]: b. p. 70-71° at 12 mm, d^{17} 0.975.

The diethylacetal of thio-β,β'-dibutyraldehyde (III) was prepared from 9 g of the diethylacetal of β-chlorobutyraldehyde and 10 g of $Na_2S \cdot 9H_2O$ in 65 ml of alcohol (160°, 4 hours); yield 2.5 g (31%).

B. p. 149-154° at 3 mm, d_4^{20} 0.9628, n_D^{20} 1.4570.
Found %: S 10.32, 10.22. $C_{16}H_{34}O_4S$. Calculated %: S 9.94.

The dimethylacetal of bromoacetaldehyde was prepared similarly to the diethylacetal from 64.5 g of vinyl acetate, 150 ml of anhydrous CH_3OH and 120 g of bromine; the yield was 69 g (55%).

B. p. 51.5-52.5° at 19 mm, d_4^{20} 1.4397, n_D^{20} 1.4460. Literature data [9]: b. p. 48-49° at 14 mm, d_4^{20} 1.4300, n_D^{20} 1.4450.

The dimethylacetal of thiodiacetaldehyde (IV). 36 g of $Na_2S \cdot 9H_2O$ and 25.5 g of the dimethylacetal of bromoacetaldehyde in 80 ml of CH_3OH were heated for 3 hours at 100° and, after working up in the usual way, we isolated (IV); the yield was 10.8 g (68%).

B. p. 115-116° at 6 mm, 125° at 10 mm, d_4^{20} 1.0781, n_D^{20} 1.4590, MR_D 53.25; calc. 53.69. Literature data [10]: b.p. 85° at 1 mm, n_D^{25} 1.4569.
Found %: C 45.96, 45.80; H 8.56, 8.42; S 15.07, 15.32. $C_8H_{18}O_4S$. Calculated %: C 45.69; H 8.63; S 15.22.

The ethylene dihydroxyacetal of bromoacetaldehyde was prepared by treating a solution of 86 g of vinyl acetate in 372 g of ethylene glycol with 160 g of bromine; the yield was 46.5 g (28%).

B. p. 63-66° at 9 mm, d_4^{20} 1.6172, n_D^{20} 1.4800, MR_D 29.34; calc. 29.52. Literature data [11]: b. p. 68-71° at 15 mm, 65-66° at 12 mm.

Found %: C 28.82, 28.77; H 4.24, 4.16; Br 47.61, 47.79. $C_4H_7O_2Br$. Calculated %: C 28.76; H 4.22; Br 47.85.

The ethylene dihydroxyacetal of thiodiacetaldehyde (V). A solution of 27 g of $Na_2S \cdot 9H_2O$ and 16.7 g of the ethylene dihydroxyacetal of bromoacetaldehyde in 100 ml of ethylene glycol was heated for 6 hours at 100° with stirring, the reaction mixture diluted 3 times with water and extracted with ether (8 times with 50 ml each). From the dry ether extracts, we isolated 3.1 g (30%) of (V).

B. p. 136.5-138° at 4 mm, d_4^{20} 1.2028, n_D^{20} 1.4945.

Found %: C 47.03, 46.87; H 7.27, 7.07; S 15.23; 15.29. $C_8H_{14}O_4S$. Calculated %: C 46.58; H 6.84; S 15.54.

SUMMARY

We synthesized 5 thiodialdehyde acetals, of which 3 were found to be effective foaming agents in the flotation of some nonferrous metal ores.

LITERATURE CITED

[1] U. S. Patent 2591289; Ch. A., 46, 5513 (1952); British Patent 662122; Ch. A., 47, 9351 (1953).

[2] S. M. Gurvich, A. K. Livshits, Trans. State Inst. Nonferrous Metals, Coll. No. 13, 58 (1956).

[3] S. M. Gurvich and A. K. Livshits, Author Cert. 105006 (1954).

[4] Synth. Org. Prep., III, 109 (1952).

[5] Fischer, Ber. 42, 1071 (1909).

[6] Clarke, Smiles, J. Chem. Soc. 95, 1000 (1909).

[7] Synth. Org. Prep., II, 67 (1949).

[8] Wohl and Fraun, Ber. 35, 1905 (1902).

[9] Bedoukian, J. Am. Chem. Soc. 66, 651 (1944).

[10] Parham, Wynberg and Ramp, J. Am. Chem. Soc. 75, 2065 (1953).

[11] Hill and Pidgeon, J. Am. Chem. Soc. 50, 2723 (1928).

Received September 11, 1956

State Institute of Research on Nonferrous Metals

AMINOACYL DERIVATIVES OF NUCLEOSIDES

1.* SYNTHESIS OF N_6-AMINOACYL AND N_6-PEPTIDE DERIVATIVES OF 3-β-D-GLUCOPYRANOSYLCYTOSINE

Z. A. Shabarova, N. I. Sokolova and M. A. Prokofyev

The chemical structure of nucleosides, the simplest structural fragments of nucleic acids, may be considered as established at the present time. As a result of the numerous investigations by Levin, Guland, Gilbert, Todd and many others, methods for synthesizing natural nucleosides and their analogs have been developed. The brilliant work by Todd et al. has definitely established the structure of natural nucleotides, methods for synthesizing them have been worked out and, consequently, a basis for a more thorough study of nucleic acids has been established.

The problem of polyaminoacyl derivatives of nucleosides and nucleotides is especially interesting. These derivatives are valuable from at least three different points of view.

Nucleosides which have the polyaminoacyl (polypeptide or peptidodiketopiperazine) group bound to the amine group of the nitrogen bases (cytosine, 5-methylcytosine, adenine, guanine) may be considered as the simplest fragments of nucleoproteins. To explain the character of the bond between protein and nucleic acid in so-called stable nucleoproteins, which was discovered and thoroughly investigated by A. N. Belozersky et al. [1], in recent years a hypothesis was put forward on the possibility of the existence of an amide bond, formed by the amino group of nitrogen bases and the terminal carboxyl group of the protein. It is well known that many facts are not covered by the theory of salt-like, ionic nucleoprotein structure, which was put forward during the period when complex protein chemistry was just starting. Some of them are: the absence of the properties of a binary electrolyte in the electrophoresis of nucleoproteins, the presence of neutral and even acid protein properties in the protein component and the discovery in a series of organs of various nucleoprotein fractions, differing from each other in stability to hydrolyzing reagents [1a]. A study of the chemistry of polyaminoacyl derivatives could clarify the structure of nucleoproteins in establishing the character of the bond between the protein and nucleic acid components.

At present the problem of the biosynthesis of protein is being discussed in the international chemical literature. Not without foundation, nucleic acids are assigned the role of an orienting "templet," on which the amino acids, connected in a certain sequence, form protein molecules [2]. One may consider that here, more or less stable chemical bonds are formed between the amino acids and peptides, on the one hand, and the nucleic acids, on the other, and that these bonds are formed from the functional groups of both components. From this point of view, polyaminoacyl derivatives of nucleosides may be considered as one of the possible types of compounds formed during biosynthesis.

Finally, it should be noted that aminoacyl derivatives of nucleosides may be of interest per se. We recall that the recently discovered antibiotic, puromycin, is the tyrosine derivative of an adenine nucleoside [3].

Investigation of aminoacyl derivatives of nucleosides is held back by the lack of methods for synthesizing them. S. E. Manoilov [4] was the only one to observe the reaction of adenine and a nucleic acid with aromatic α-amino acids, which gave N_6-tyrosine and some other derivatives of adenine and nucleic acids. Manoilov's method, however, is not a preparative one.

We decided, as our most immediate aim, to develop a method for synthesizing aminoacyl and peptide

* For the previous report see Proc. Acad. Sci. USSR, 109, 340 (1956).

derivatives of nucleosides. This work describes the synthesis of such derivatives of a cytosine nucleoside.

As we showed previously, aminoacyl derivatives of 2- and 4-aminopyrimidines may be prepared from aminopyrimidines by one of the following methods: 1) haloacylation followed by substitution of the halide in the side chain with an amino group; 2) acylation of substituted amino acids with an acid halide and 3) acylation of substituted amino acids with mixed anhydrides. In this way, various aminoacyl and peptide derivatives of 2- and 4-aminopyrimidines were prepared [5-7]. However, derivatives of cytosine and its analogs, in which the pyrimidine nucleus was bound to peptides, consisting of various amino acids, could not be prepared by any of these methods.

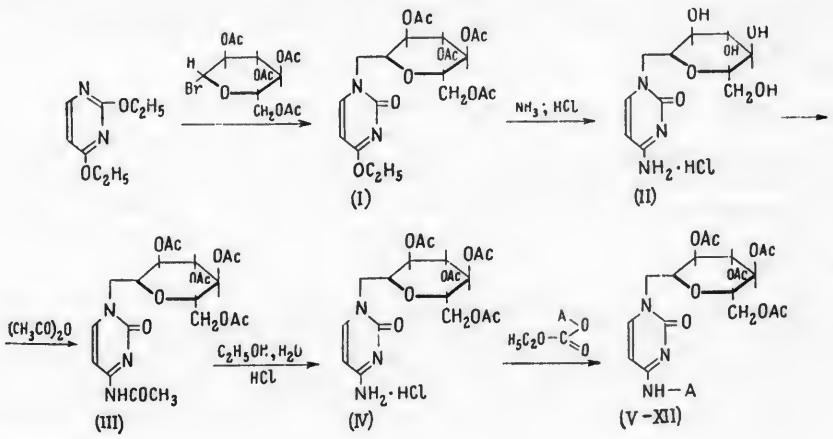
Of the methods listed above, we considered the method of acylation with mixed anhydrides as the most suitable for the synthesis of peptide derivatives of 4-aminopyrimidines. The preparation of mixed peptide anhydrides is described in the literature. By using these acylating reagents, di-, tri- and polypeptide derivatives of aminopyrimidines could be prepared simultaneously. But, as is known, mixed anhydrides of amino acids and peptides are stable only at low temperatures (0°). Due to this, aminoacyl derivatives could be synthesized, in the case of 4-aminopyrimidines, only by using those aminopyrimidines whose amino group hydrogen was especially labile, as, for example, in the case of kyanmitin [6]. The reaction did not proceed with cytosine.

However, it was observed, earlier, that acetylation of cytosine nucleosides [8] proceeded much more readily than the acetylation of cytosine [9]. One could assume that aminoacylation of cytosine nucleoside would also proceed much more readily than that of cytosine itself and that aminoacylation of cytosine nucleoside with mixed anhydrides of amino acids and peptides would give the corresponding aminoacyl and peptide derivatives. Our assumption was justified.

We used 3-β-D-glucopyranosylcytosine (II) as the starting nucleoside. It differed only in the sugar structure from natural cytidine nucleoside (3-β-D-ribofuranosylcytosine).

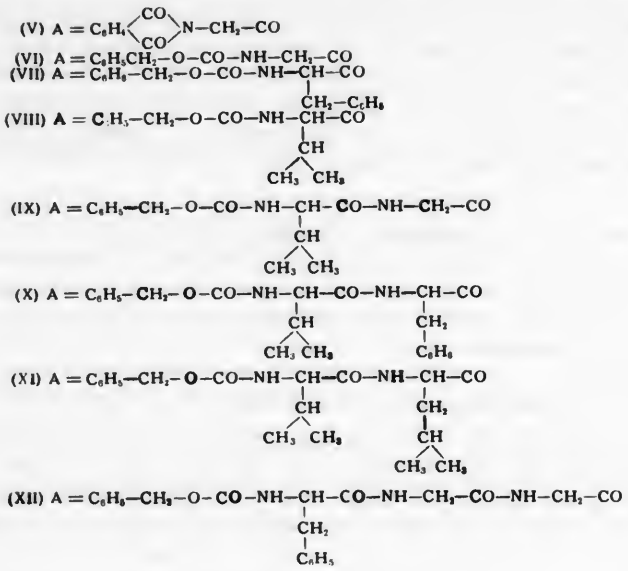
3-β-D-Glucopyranosylcytosine (II) was prepared from 2,6-diethoxypyrimidine and acetobromoglucose and was readily acetylated with acetic anhydride at room temperature [8]. When the pentacetyl derivative (III) thus obtained was heated for a short time with 96% ethyl alcohol in the presence of a small amount of concentrated HCl, it lost one acetyl group and was converted into 3-β-D-tetraacetylglucopyranosylcytosine (IV). The latter was readily acylated at a low temperature with mixed anhydrides of various substituted amino acids and peptides to give the corresponding N_6-aminoacyl- and N_6-peptidonucleosides (V–XII) (in 30 to 50% yields). The reaction was carried out in an anhydrous organic solvent (dioxane, chloroform) at 0-5° in vacuum. It should be noted that in this case, when an amino acid or peptide with a branched carbon chain was introduced into the reaction the N_6-aminoacyl- nucleoside yields fell. Thus the yield of N_6-cbz* -valylleucylnucleoside was only 15%.

The general reaction scheme may be represented in the following way.



where: Ac = CH_3CO

* cbz is carbobenzoxy ($C_6H_5CH_2OCO$).



EXPERIMENTAL

1,2-Dihydro-2-keto-6-ethoxy-3-tetraacetyl-β-D-glucopyranosylpyrimidine (I) [8]. In a test tube, fitted with a calcium chloride tube, was placed 2 g of freshly prepared bromotetraacetyl-β-D-glucose [10] and 2 g of 2,6-diethoxypyrimidine [11]. The evolution of bubbles of ethyl bromide was observed and this increased considerably on putting the reaction mixture in vacuum. The mixture was heated at 30° (at 15 mm) for 1 hour and at 65° (at 765 mm) for 20 hours. To the cooled, crystalline mass was added 5-7 ml of anhydrous ether and the precipitate filtered off, washed with cold anhydrous ether and recrystallized twice from anhydrous ethyl alcohol. The yield was 1.25 g (23%). The m. p. was 205°. Literature data: m. p. 206° [8].

The hydrochloride of 3-β-D-glucopyranosylcytosine (II) [12]. A solution of 3.5 g of (I) in 20 ml of anhydrous ethyl alcohol, saturated with dry ammonia at 0°, was heated for 40 hours in an autoclave at 90°. After cooling, the reaction mixture was evaporated down under reduced pressure. The residual oil dissolved on heating in 100 ml of 95% ethyl alcohol. The solution was decolorized by boiling with charcoal and acidified to congo with conc. HCl. The precipitate, which formed in the cold, was filtered off and washed with cold, anhydrous alcohol. The yield was 2 g (90%), the m. p. was 199°. Literature data: m. p. 199° [12]. Absorption in the UV in 96% ethyl alcohol: λ_{max} 275 mμ (ε 5400).

Found %: C 38.64; H 5.11; N 13.45. $C_{10}H_{15}O_6N_3 \cdot HCl$. Calculated %: C 38.77; H 5.17; N 13.57.

Pentaacetyl-3-β-D-glucopyranosylcytosine (III) [8]. A solution of 1.5 g of (II) in 6 ml of acetic anhydride and 7.5 ml of pyridine was left at room temperature for a day and then poured onto 30 g of crushed ice with stirring. The amorphous precipitate was filtered off and recrystallized twice from ethyl alcohol. The yield was 2 g (85.5%). The m. p. was 225°. Literature data: m. p. 225° [8]. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300-302 mμ (ε 3800, 1700).

The hydrochloride of 3-β-D-tetraacetylglucopyranosylcytosine (IV). A solution of 1.8 g of (III) in 80 ml of 96% ethyl alcohol was boiled for 1 hour with 0.5 ml of conc. HCl and evaporated to dryness in vacuum. To the gel-like residue was added 20 ml of anhydrous benzene, which was evaporated to dryness in vacuum. The operation was repeated 5 times. The residue was a white, friable powder. The yield was 1.43 g (80%). The m. p. was 202°. Absorption in the UV in 96% ethyl alcohol: λ_{max} 275 mμ (ε 2500). Before analysis, the substance was dried in vacuum at 110° over P_2O_5 for 20 hours.

Found %: C 42.25; H 5.50; N 8.15. $C_{18}H_{24}O_{10}N_3Cl \cdot 2H_2O$. Calculated %: C 42.1; H 5.45; N 8.19.

After drying the substance under the same conditions at 140°, it lost only one molecule of water.

Found %: C 43.78; H 5.27. $C_{18}H_{24}O_{10}N_5Cl \cdot H_2O$. Calculated %: C 43.63; H 5.25.

N_6-Phthalylglycyl-3-β-D-tetraacetylglucopyranosylcytosine (V). 0.04 ml of ethyl chlorocarbonate was added to a solution of 0.08 g of phthalylglycine in 4 ml of chloroform and 0.1 ml of tributylamine, cooled to 0°. The reaction mixture was kept at 0° for 15 minutes and then a solution of 0.2 g of (IV) in 4 ml of dioxane and 0.1 ml of tributylamine was added to it. The solution was put into vacuum for 30 minutes and then left in the cold for a day. After evaporation in vacuum, 5 g of crushed ice was added to the oil. The precipitate was filtered off and washed with 0.1 N NaOH, 0.1 N HCl and water. The yield of (V) was 0.15 g (60%). The substance was purified by reprecipitation from benzene with petroleum ether. Decomp. point 152-154°. Absorption in the UV in 96% ethyl alcohol: λ_{max} 240, 298 mμ (ε 7300, 2550).

Found %: C 53.43; H 4.29; N 9.01. $C_{28}H_{28}O_{13}N_4$. Calculated %: C 53.50; H 4.46; N 8.92.

N-cbz-Glycyl-3-β-D-tetraacetylglucopyranosylcytosine (VI). 0.06 ml of tributylamine and 0.024 ml of ethyl chlorocarbonate were added to a solution of 0.052 g of cbz-glycine in 3 ml of anhydrous dioxane, cooled to 0°. The reaction mixture was kept at 0° for 15 minutes and then a solution of 0.125 g of (IV) in 5 ml of dioxane and 0.036 ml of 0.5 N NaOH was added to it. The reaction mixture was put into vacuum for 10-15 minutes (the evolution of bubbles of CO_2 was observed) and then left at 5° for a day. After evaporation to dryness in vacuum, 5 ml of cold water was added to the oil. The precipitate was washed with 0.1 N NaOH, 0.1 N HCl and water. The substance was dissolved in 3-5 ml of chloroform. The solution was filtered and dried with Na_2SO_4 and anhydrous petroleum ether added to it. The precipitate formed was filtered off. The yield was 0.054 g (34%). Decomp. point 119-121°. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 8200, 3300). The substance was dried in vacuum over P_2O_5 at 70° for 20 hours.

Found %: C 53.22; H 5.32; N 8.87. $C_{28}H_{32}O_{13}N_4$. Calculated %: C 53.16; H 5.1; N 8.86.

N_6-cbz-Phenylalanine-3-β-D-tetraacetylglucopyranosylcytosine (VII). 0.06 ml of tributylamine and 0.024 ml of ethyl chlorocarbonate were added to a solution of 0.078 g of cbz-phenylalanine in 3 ml of dry chloroform, cooled to 0°. The mixture was left for 15 minutes at 0° and a solution of 0.125 g of (IV) in 5 ml of dry chloroform and 0.06 ml of tributylamine was added to it. The reaction mixture was put into vacuum for 15-20 minutes. The following day the reaction mixture was washed with water, 0.1 N NaOH, 0.1 N HCl and water. After drying the solution with sodium sulfate, 20 ml of anhydrous petroleum ether was added to it. The precipitate formed was reprecipitated once. The yield was 0.083 g (55%). Decomp. point 143-145°. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 6900, 3000). The substance was dried in vacuum over P_2O_5 at 70° for 20 hours before analysis.

Found %: C 58.55; H 5.44; N 7.77. $C_{35}H_{38}O_{13}N_4$. Calculated %: C 58.17; H 5.26; N 7.75.

N_6-cbz-Valyl-3-β-D-tetraacetylglucopyranosylcytosine (VIII). This was prepared as described above from cbz-valine and (IV). Yield 26%. Decomp. point 92°. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 9400, 3800). Before analysis, the substance was dried in vacuum over P_2O_5 at 70° for 20 hours.

Found %: C 55.2; H 5.83; N 8.10. $C_{31}H_{38}O_{13}N_4$. Calculated %: C 55.2; H 5.64; N 8.31.

N_6-cbz-Valylglycyl-3-β-D-tetraacetylglucopyranosylcytosine (IX). 0.06 ml of tributylamine and 0.024 ml of ethyl chlorocarbonate were added to a solution of 0.077 g of cbz-valyl-glycine in 3 ml of dry chloroform, cooled to 0°. After 15 minutes (0°), a solution of 0.125 g of (IV) in 5 ml of anhydrous dioxane and 0.06 ml of tributylamine was added to the mixed anhydride. The reaction mixture was put in vacuum for 30 minutes and then left overnight. Crushed ice was added to the oil remaining after evaporation. The thickened mass was ground with 10% sodium carbonate solution and washed with water, 0.1 N HCl and again with water. The precipitate formed was dissolved in 10 ml of chloroform, dried with sodium sulfate and precipitated with petroleum ether. The yield was 0.072 g (40%). Decomp. point 120-123°. The substance was insoluble in cold water and petroleum ether; it dissolved in hot water and the usual organic solvents. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 1100, 3500). Before analysis, the substance was dried for 20 hours at 70° over P_2O_5 in vacuum.

Found %: C 53.92; H 5.88; N 10.02. $C_{33}H_{41}O_{14}N_5$. Calculated %: C 54.17; H 5.74; N 9.58.

N_6-cbz-Valylphenylalanyl-3-β-D-tetraacetylglucopyranosylcytosine (X). This was prepared as described above for (IX) from the mixed anhydride of cbz-valylleucine and (IV) in chloroform. The yield was 40%. Decomp.

point 128-130° (from a mixture of chloroform and petroleum ether). The substance was insoluble in cold water and soluble in hot water and the usual organic solvents. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 9000, 3700). The substance was dried in vacuum over P_2O_5 at 70° for 20 hours before analysis.

Found %: C 58.30; H 5.88; N 8.93. $C_{40}H_{47}O_{14}N_5$. Calculated %: C 58.46; H 5.77; N 8.53.

N_6-cbz-Valylleucyl-3-β-D-tetraacetylglucopyranosylcytosine (XI). This was prepared as described above for (IX) from the mixed anhydride of cbz-valylleucine and (IV) in chloroform. The yield was 15%. Decomp. point 112°. The substance was readily soluble in organic solvents; it was insoluble in cold water and petroleum ether. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 9000, 3400). Before analysis, the substance was dried in vacuum over P_2O_5 at 70° for 20 hours.

Found %: N 8.73. $C_{37}H_{49}O_{14}N_5$. Calculated %: N 8.86.

N_6-cbz-Phenylalanylglycylglycine-3-β-D-tetraacetylglucopyranosylcytosine (XII). To the mixed anhydride, prepared from 0.12 g of cbz-phenylalanylglycylglycine in 5 ml of anhydrous dioxane, was added 0.15 g of (IV) in 0.5 ml of water, containing 0.012 g of NaOH. The reaction mixture was put in vacuum for 30 minutes and then left for a day at 10°. Ether was added to the residue left after evaporation in vacuum. The oil was separated and poured into ice. The precipitate was washed with 0.1 N NaOH, 0.1 N HCl and water and reprecipitated from alcohol with ether. The yield of (XII) was 0.1 g (42%). Decomp. point 139-140°. Absorption in the UV in 96% ethyl alcohol: λ_{max} 250, 300 mμ (ε 4450, 2050). Before analysis, the substance was dried in vacuum over P_2O_5 at 75° for 20 hours.

Found %: C 54.68; H 5.47; N 9.65. $C_{39}H_{44}O_{15}N_6 \cdot H_2O$. Calculated %: C 54.80; H 5.38; N 9.83.

Preparation of cbz-peptides [13]

Methyl ester of cbz-valylphenylalanine. 2.4 ml of tributylamine and 0.76 ml of ethyl chlorocarbonate were added to a solution of 2.51 g of cbz-valine in 25 ml of anhydrous ether, cooled to 0°. After 15 minutes (0°), a solution of 2.15 g of the methyl ester of phenylalanine hydrochloride in 10 ml of ethyl alcohol and 2.4 ml of tributylamine was added to the mixed anhydride. There was a vigorous evolution of CO_2. After 2 hours, the precipitate was filtered off and dissolved in 15 ml of ether. The ether solution was washed with water, 1 N HCl, 10% sodium carbonate solution and again with water. The precipitate was filtered off and reprecipitated from alcohol with water. The yield was 3.56 g (87%). The m. p. was 146°.

Found %: N 7.48. $C_{23}H_{28}O_5N_2$. Calculated %: N 7.56.

cbz-Valylphenylalanine. A solution of 3.56 g of the methyl ester of cbz-valylphenylalanine in 30 ml of 95% ethyl alcohol and 9 ml of 1 N NaOH was heated for 4 hours at 37°. The hydrolyzate was acidified to congo with hydrochloric acid and diluted with 7-8 times the amount of water. The precipitate formed was dissolved in ether. The ether solution was washed with water and extracted with 1 N NaOH. After neutralization, the alkaline solution was left for 2 hours at 0°. The precipitate was filtered off and recrystallized from ethyl alcohol. The m. p. was 150°. Literature data: m. p. 142° [13].

Found %: N 7.00. $C_{22}H_{26}O_5N_2$. Calculated %: N 7.04.

By the same method we prepared the following cbz-dipeptide esters and cbz-dipeptides.

The methyl ester of cbz-valylglycine. Yield 70%. M. p. 128°.

Found %: N 8.6. $C_{16}H_{22}O_5N_2$. Calculated %: N 8.69.

cbz-Valylglycine. Yield 68%. M. p. 146°. Literature data: m. p. 138-139° [13].

Found %: N 9.00. $C_{15}H_{20}O_5N_2$. Calculated %: N 9.09.

The methyl ester of cbz-valylleucine. Yield 66%. M. p. 112°.

Found %: N 7.37. $C_{20}H_{30}O_5N_2$. Calculated %: N 7.40.

cbz-Valylleucine. Yield 58%. M. p. 143°. Literature data: m. p. 135° [13].

Found %: N 7.50. $C_{19}H_{28}O_5N_2$. Calculated %: N 7.69.

SUMMARY

Using 3-β-D-glucopyranosylcytosine as the example, it was shown that the reaction of cytosine nucleoside with mixed anhydrides of N-substituted amino acids and peptides may serve as a method for synthesizing their aminoacyl and peptide derivatives. A series of such derivatives was synthesized.

It was noted that the amino group in 3-β-D-glucopyranosylcytosine was more reactive than that in cytosine itself.

LITERATURE CITED

[1] A. N. Belozersky, Biochemistry 1, 255 (1936); A. N. Belozersky and I. I. Dubrovskaya, Biochemistry 1, 665 (1936).

[1a] B. Keil, M. Hrubesova, Chem. Listy, 1955, 274.

[2] A. R. Todd, J. Roy. Soc. Arts, 1955, 769.

[3] C. W. Waller, P. W. Fryth, B. L. Hutchings, J. H. Williams, J. Am. Chem. Soc. 75, 2025 (1953).

[4] S. E. Manoilov, Proc. Acad. Sci. USSR 67, 329 (1949).

[5] M. A. Prokofyev , Z. A. Rumyantseva, D. Ya. Rosina, E. D. Sopach, Sci. Repts, Moscow State Univ. No. 151, Vol. VIII, 349 (1951).

[6] M. A. Prokofyev, Z. A. Shabarova, Proc. Acad. Sci. USSR 95, 997 (1954).

[7] M. A. Prokofyev, Z. A. Shabarova, E. G. Antonovich, J. Gen. Chem. 25, 397 (1955).*

[8] G. E. Hilbert, E. F. Jansen, J. Am. Chem. Soc. 58, 60 (1936).

[9] H. L. Wheeler, T. B. Johnson, Am. Chem. J. 29, 501 (1903).

[10] C. G. Jeremias, G. B. Lucas, C. A. Mackenzie, J. Am. Chem. Soc. 70, 2598 (1948).

[11] G. E. Hilbert, T. B. Johnson, J. Am. Chem. Soc. 52, 2001 (1930).

[12] J. Fox, L. Goodman, J. Am. Chem. Soc. 73, 3257 (1951).

[13] J. W. Davis, Ann. Chim. 9, 399 (1954).

Received October 9, 1956

Moscow State University

THE SYNTHESIS OF THIAZOLIDONE DERIVATIVES OF BIOLOGICAL INTEREST

VI. THE CONDENSATION REACTION OF MONOCHLOROACETIC ACID AND THIOSEMICARBAZIDE IN THE PRESENCE OF ALDEHYDES

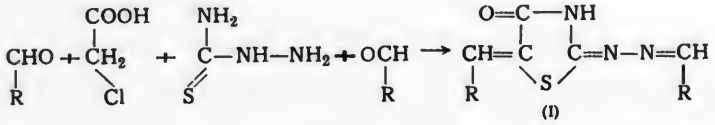
E. V. Vladzimirskaya

Derivatives of thiazolidine-2,4-dione-2-hydrazone, substituted in both the 2' and the 5 position, are formed in one stage by the condensation of monochloroacetic acid and thiosemicarbazones in the presence of aldehydes [1, 2]. To obtain derivatives of thiazolidine-2,4-dione-2-hydrazone containing similar arylidene groups in the two above-mentioned positions, it was necessary to introduce both an aromatic aldehyde and its thiosemicarbazone in the condensation reaction. As is known, however, thiosemicarbazones of aldehydes are obtained by the direct reaction of an aldehyde with thiosemicarbazone. This suggested the possibility of obtaining a substance with the above-mentioned structure by introducing unsubstituted thiosemicarbazide into the condensation reaction instead of thiosemicarbazone. The experiments we carried out confirmed our suggestion, since when we condensed monochloroacetic acid and thiosemicarbazide in the presence of excess aldehydes we obtained a number of derivatives of thiazolidine-2,4-dione-2-hydrazone which had not previously been described in the literature.

To investigate the chemistry of the reaction taking place during this condensation, we decided on the use of the following aldehydes: benzaldehyde, anisaldehyde, salicylaldehyde, o-chlorobenzaldehyde, m-nitrobenzaldehyde and p-dimethylaminobenzaldehyde. In addition, for purposes of comparison, we introduced an aldehyde of the heterocyclic series – furfural – into the condensation reaction.

To ensure the formation of the thiosemicarbazone in the initial stage of the reaction the solution of thiosemicarbazide in glacial acetic acid was boiled with excess aldehyde for 10 minutes, after which an amount of monochloroacetic acid, equivalent to the amount of thiosemicarbazide, was added to the reaction mixture. When salicylaldehyde was used for the condensation reaction, the formation of a copious precipitate was observed within a few minutes of the addition of monochloroacetic acid. In all other instances the precipitate was formed after continuous boiling or when the reaction mixture had been cooled.

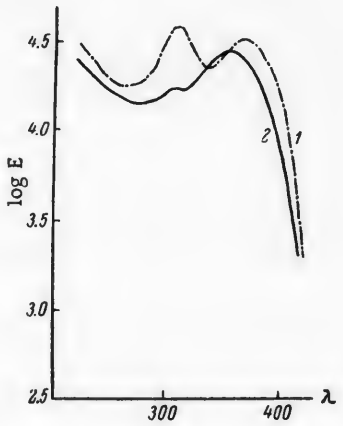
The ultimate analysis of the condensation products we obtained showed that the reaction proceeded according to the equation



(I)

when benzaldehyde, anisaldehyde, o-chlorobenzaldehyde and m-nitrobenzaldehyde were used. A similar reaction carried out with the use of salicylaldehyde leads to the formation of thiazolidine-2,4-dione-2-salicylidenehydrazone (instead of the expected 5,2"-disalicylidene derivative). The substance obtained is almost completely insoluble in glacial acetic acid and is precipitated from the reaction mixture almost immediately after its formation. In consequence, its subsequent condensation with salicylaldehyde in the 5 position is impossible.

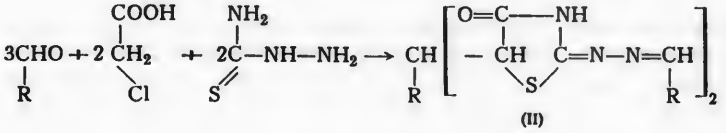
The anomalous reaction in the case of salicylaldehyde indicates the mechanism of the condensation reaction of monochloroacetic acid and thiosemicarbazide in the presence of excess aldehydes. The condensation reaction takes place in three successive stages: 1) the formation of thiosemicarbazones by the reaction of the aldehydes and thiosemicarbazide, 2) the formation of a thiazolidine ring (by the reaction of monochloroacetic acid and thiosemicarbazones) and the formation of 2" derivatives of thiazolidine-2,4-dione-2-hydrazone, 3) the condensation of the thiazolidine compounds formed with the aldehydes in the 5 position and the formation of 5-derivatives.



Absorption spectra of pseudothiohydantoin derivatives.
1) 5,2"-Di-p-anisylidene derivative. 2) 5,2"-Di-o-chlorobanzylidene derivatives.

To confirm the correctness of our proposed system for the above-mentioned reaction mechanism we carried out two additional condensations commencing with the separately prepared thiosemicarbazone of salicylaldehyde. We obtained this thiosemicarbazone by Freund and Schander's method [3]; its physico-chemical properties corresponded to literature data. The substance obtained was introduced in the condensation reaction with monochloroacetic acid in the presence of salicylaldehyde and, in addition, for purposes of comparison, in the presence of m-nitrobenzaldehyde. In both instances we obtained the monosalicylidene-derivative of thiazolidine-2,4-dione-2-hydrazone (instead of the expected 5-derivatives). Because of its insolubility the substance obtained did not enter into the reaction with salicylaldehyde and m-nitrobenzaldehyde; this agrees with the above-mentioned data on the condensation reaction of monochloroacetic acid and thiosemicarbazide in the presence of excess salicylaldehyde.

The investigations we carried out on furfural and also on p-dimethylaminobenzaldehyde indicate that in this instance the condensation reaction takes place according to a different system. These aldehydes can each add two molecules of the 2"-derivatives of thiazolidine-2,4-dione-2-hydrazone according to the equation



(II)

Similar substances – derivatives of pseudothiohydantoin, in the molecule of which there are 3 aldehyde groups, – were described by us for the first time [1]. It should also be mentioned that similar substances – rhodanine derivatives – were obtained by Bradsher and his co-workers [4].

We [5] also described substances of a similar structure to 5-p-anisylidene- and 5-o-chlorobenzylidene derivatives in which, however, there is a p-acetaminobenzylidene grouping in the 2"-position. The analogous structure of these substances is reflected in the similarity of their absorption spectra in the ultraviolet region. All these 4 substances have characteristic maxima on their absorption curves. The absorption maxima (figure) in the ≅365 mμ region are characteristic for 5-arylidene derivatives while the maxima in the ≅310 mμ region are characteristic for pseudothiohydantoin itself, the derivatives of which include the substances we investigated. From a comparison of the absorption spectra of the substances we synthesized and those mentioned in the communication [5] it follows that the p-acetaminobenzylidene grouping displaces the principal maximum to some extent and also the long-wave region of the absorption spectra. In addition, it should be pointed out that in the case of 5-o-chlorobenzylidenethiazolidine-2,4-dione-2-p-acetaminobenzylidenehydrazone the absorption spectra in the ≅310 mμ region form wide bands, as a result of which the maxima in this region are poorly developed.

TABLE 1

Condensation Products of Monochloroacetic Acid and Thiosemicarbazide in the Presence of Aldehydes

Name of the compound	Formula	Yield (as %)	Melting point	N Content (as %) found	N Content (as %) calculated
5-Benzylidenethiazolidine-2,4-dione-2-benzylidenehydrazone	$C_{17}H_{13}ON_3S$ (I, R = C_6H_5)	75	283°	13.76	13.67
5-p-Anisylidenethiazolidine-2,4-dione-2-p-anisylidenehydrazone	$C_{19}H_{17}O_3N_3S$ (I, R = $CH_3OC_6H_4$)	53	241	11.50	11.44
5-o-Chlorobenzylidenethiazolidine-2,4-dione-2-o-chlorobenzylidenehydrazone	$C_{17}H_{11}ON_3Cl_2S$ (I, R = ClC_6H_4)	55	275-276 (decomp.)	11.20	11.17
5-m-Nitrobenzylidenethiazolidine-2,4-dione-2-m-nitrobenzylidenehydrazone	$C_{17}H_{11}O_5N_5S$ (I, R = $O_2NC_6H_4$)	64	265-266	17.56	17.63
5-Furfurylidene-bis-(thiazolidine-2,4-dione-2-furfurylidenehydrazone)	$C_{21}H_{16}O_5N_6S_2$ R = C_4H_3O	38.2	200 (decomp.)	16.93*	16.93
5-p-Dimethylaminobenzylidene-bis-(thiazolidine-2,4-dione-2-p-dimethylaminobenzylidenehydrazone)	$C_{33}H_{37}O_2N_9S_2$ [II, R = $(CH_3)_2NC_6H_4$]	25.3	230	19.59**	19.23
Thiazolidine-2,4-dione-2-salicylidenehydrazone	$C_{10}H_9O_2N_3S$	32	254-255	17.97	17.86

* C 50.70; C 50.80
H 3.35; H 3.25.

** C 60.40; C 60.43
H 5.51; H 5.60.

All the substances we synthesized are fluorescent (when they are illuminated by the ultraviolet rays of a Bach lamp). Their silver salts, which can easily be obtained by precipitating with silver nitrate from alcoholic solutions of the corresponding compounds, are more strongly fluorescent.

5,2"-Disubstituted derivatives of the thiazolidine-2,4-dione-2-hydrazone have weakly acidic properties; they are practically insoluble in typical organic solvents (ether, chloroform, benzene). Furfurylidene- and p-dimethylaminobenzylidene derivatives, containing three aldehyde groups in their molecules, have more clearly expressed acidic properties and are distinguished from diarylidene derivatives by their fairly good solubility in organic solvents. It should be pointed out that alkaline solutions of the p-dimethylaminobenzylidene derivative (in solutions of NaOH, Na_2CO_3 and $NaHCO_3$, and also in pyridine) are characterized by a blue fluorescence.

The derivatives of thiazolidene-2,4-dione-2-hydrazone which we synthesized, actively restrain the growth of tubercular bacilli .

EXPERIMENTAL

5,2"-Diarylidene derivatives of thiazolidine-2,4-dione-2-hydrazone. 1.8 g (0.02 mole) of thiosemicarbazide, 0.04-0.05 mole of aldehyde and 40 ml of glacial acetic acid were boiled for 10 minutes with a reflux condenser. 1.9 g (0.02 mole) of monochloroacetic acid was added to the transparent solution obtained and boiling was continued for a further 50 minutes. An aqueous solution of sodium acetate was added to the cooled reaction mixture; the precipitate was then filtered, washed with water and dried. The dried yellow condensation products were recrystallized from glacial acetic acid and analyzed.

Condensation products of furfural and p-dimethylaminobenzaldehyde. The condensation reaction was carried out in a similar manner to that described above. In the case of furfural, however, the reaction mixture was boiled for 2 hours, a precipitate only being formed after dilution with an aqueous solution of sodium acetate.

The condensation product with furfural (greenish color) was recrystallized from dilute alcohol and the condensation product with p-dimethylaminobenzaldehyde (orange color) from chloroform.

Thiazolidine-2,4-dione-2-salicylidenehydrazone. The condensation reaction of thiosemicarbazide and monochloroacetic acid in the presence of salicylaldehyde was carried out as described above. After the reaction mixture had been boiled for several minutes the condensation product was precipitated as long needles. The m.p. was 254-255° (from glacial acetic acid); this corresponds to literature data [6] for thiazolidine-2,4-dione-2-salicylidenehydrazone, obtained by condensing monochloroacetic acid and salicylaldehyde in an alcoholic medium.

We obtained an identical compound by boiling equimolecular amounts (12 millimole each) of salicylaldehyde (or m-nitrobenzaldehyde, respectively), monochloroacetic acid, salicylaldehyde thiosemicarbazone and 25 ml of glacial acetic acid for 1 hour. The yield of the condensation product was 74-95%.

SUMMARY

1. The condensation reaction of monochloroacetic acid and thiosemicarbazide in the presence of benzaldehyde, o-chlorobenzaldehyde, p-anisaldehyde and m-nitrobenzaldehyde leads to the formation of diarylidene derivatives of thiazolidine-2,4-dione-2-hydrazone.

2. In a similar condensation reaction with salicylaldehyde, the monosalicylidene derivative of thiazolidine-2,4-dione-2-hydrazone is formed.

3. Condensation with the use of furfural and p-dimethylaminobenzaldehyde leads to the formation of derivatives of thiazolidine-2,4-dione-2-hydrazone, containing three aldehyde groups in their molecules.

LITERATURE CITED

[1] E. V. Vladzimirskaya, N. M. Turkevich, J. Gen. Chem. 25, 2150 (1955).*

[2] E. V. Vladzimirskaya, J. Gen. Chem. 27, 1345 (1957).*

[3] M. Freund, A. Schander, Ber. 35, 2602 (1902).

[4] C. K. Bradsher, F. C. Brown, R. J. Grantham, J. Am. Chem. Soc. 73, 5377 (1951).

[5] N. M. Turkevich, E. V. Vladzimirskaya, J. Gen. Chem. 27, 1348 (1957).*

[6] P. Chabrier, E. Cattelain, Bull. Soc. Chim. (5) 17, 48 (1950).

Received September 11, 1956

Lvov Medical Institute

* Original Russian pagination. See C. B. Translation.

THE REPRESENTATION OF THE PERIODIC SYSTEM OF THE ELEMENTS

A. M. Vasilyev*

The periodic law formulated by D. I. Mendeleev is one of the greatest achievements of chemistry. Engels' well-known words are: "Mendeleev, by unconsciously employing the Hegelian law of the transformation of quantity into quality, achieved a scientific advance which may be equated without hesitation with the discovery of Leverrier who calculated the orbit of the planet Neptune before it was discovered."

D. I. Mendeleev's prediction of the existence of new, still undiscovered elements was an act of great daring: his correction of the atomic weights of several elements, and in particular uranium, required perhaps still greater courage. These bold pronouncements, based on his firm confidence in the truth of the law he had formulated, were strikingly confirmed by later investigations.

Far be it from me to consider the principle of "ipse dixit" as immutably true, but Mendeleev himself, in his Faraday lecture in London in 1889, said: "As a recent scientific generalization which has nevertheless stood up to investigations in the laboratory, and as an instrument of thought which has not yet undergone modification, the periodic law awaits not only additions but also improvements, detailed development, and fresh forces. All these are sure to come. . ." Since its conception, this law has not remained a fixed formula. The additions and improvements which Mendeleev expected were introduced, and their addition has continued up to the present time over the entire period of 85 years since the law was first formulated. Eleven years after the above-mentioned Faraday lecture, Mendeleev himself enthusiastically welcomed the introduction of the zero group, and 15 years after this was done, he indicated the possibility of discovering the pre-hydrogens.

Work in this direction is still continuing today. The atomic number, atomic structure, radioactivity, isotopes and isobars have all fitted into the framework of the periodic law and do not transgress it. Moreover, all these new discoveries which have had such a revolutionary effect on our whole conception of the world cannot yet fully explain all that we can extract from Mendeleev's law and the periodic table of the elements.

The numerous attempts to arrange the natural system of the elements in a particular manner demonstrate that, in the final analysis, the best arrangement is still the so-called "short" table of Mendeleev himself. By now, many expert opinions of Mendeleev's periodic system have been voiced by a number of investigators, and it is not accidental, of course, that the basis has been this "short" table.

At this point I wish to call attention to certain points which, for some reason or other, are passed over. In doing so, I assume that if there are not sufficient grounds for changing the arrangement of the elements in the table drawn up by Mendeleev himself, it is unnecessary to make any such change. Tables of the periodic system put forward as school textbooks should be considered from this viewpoint, although such an approach might appear formalistic.

The most widely distributed table of the periodic system at the present time is that published by the State Chemical Press in 1947 (under the signature of Prof. B. N. Nekrasov). In the third Group of this table the elements are arranged in the following manner (for the time being I am disregarding the other Groups):

Series	III Group
1	. . . . .
2	B
3	Al
4	Sc
5	Ga
6	Y

* Deceased.

The chief proof of Mendeleev's law is the prediction of the new elements scandium, gallium and germanium. He called scandium ekaboron, but the arrangement of the elements shown above provides no basis for identifying ekaboron with scandium; in this table there is no association whatsoever between scandium and boron, and with such an arrangement ekaboron should be called aluminum. A similar arrangement of the elements was given in the third edition of "A Short Handbook of Chemistry" by V. I. Perelman (1954).

In another edition of the table of the periodic system of the elements (under the signature of Prof. Vict. I. Spitsyn) the elements of Group III are arranged in the following manner:

Series	III Group
1	. . . . .
2	B
3	Al
4	Sc
5	Ga
6	Y

Again, in this instance, it is wrong to identify eka-aluminum with gallium: gallium has no association with any of the preceding elements of this Group, including aluminum. This is made all the more conspicuous by the exceptional similarity between the properties of aluminum and gallium, a similarity which was one of Mendeleev's striking predictions. When the elements are arranged in this manner, eka-aluminum becomes scandium.

The incorrect – in my opinion – position of ekaboron or eka-aluminum in these tables is a concealed and relatively unfounded revision of Mendeleev's opinions motivated undoubtedly by the desire to distinguish the main and the secondary sub-groups.

After the well-deserved triumph of Mendeleev's opinions which followed the discovery of scandium, gallium and germanium, the first to give the periodic law the appreciation it merited were the English chemists. At first the discovery of argon caused some difficulty and even Mendeleev himself was somewhat disconcerted. The discovery of the other inert gases – helium, neon, krypton and xenon – soon after that of argon, however, provided a new confirmation of the periodic law, and since this discovery was made by English chemists headed by Ramsey, the latter remained followers of the great Russian chemist, at least until the work of Moseley was published.

The attitude of the French chemists to Mendeleev's law has always been somewhat restrained, although their numbers include Champcourtois, who came fairly close to the natural system of the elements and Lecoq de Boisbaudran, who discovered gallium. For example, about 1905, one of the most eminent French chemists, Moissan, in his "Traite de chimie minerale" arranged the elements according to a system of his own and mentioned the natural system in extremely guarded terms. Twenty years later, Pascal, who published what was virtually a second edition of the same handbook under the same title, followed Moissan's example. His remarks in the introduction to this handbook are very revealing: the natural classification "does not always satisfy the chemist who likes to compare substances having the maximum possible number of analogous properties."

The attitude of the German chemists was ambiguous. On the one hand, they wished to prove the absolute and undisputed priority of Lothar Meyer, while, on the other hand, Meyer reduced these attempts to prove his priority to nothing when he declared in 1870 after Mendeleev's statements: "It would be rash to alter the accepted atomic weights on the basis of so uncertain a starting point. Generally speaking it would be wrong at the present time either to rely too strongly on arguments of this type or to expect them to yield such definite results as the determination of specific heat or vapor density ...." In his book, "The Foundations of Physical Chemistry," published in Stuttgart in 1909, Trauber wrote: "In the attached table, the elements are arranged, with the inclusion of certain new additions, in accordance with Lothar Meyer's plan. Mendeleev has a similar arrangement." (Page 50). Incidentally, the words "....with the inclusion of certain new additions..." refer to the inclusion in the table of scandium, gallium and germanium, but make no mention of the fact that these elements are Mendeleev's ekaboron, eka-aluminum and ekasilicon. The arrangement of the elements in the "attached" table gives the following (groups, series and periods are not mentioned in Trauber's book):

He	Li	Be	B	C		N			. . .
Ne	Na	Mg	Al	Si		P			. . .
Ar	K	Ca	Sc	Ti		V			. . .
Kr (!)	Cu	Zn	Ga		Ge		As		. . .
Xe (!)	Rb	Sr	Y	Zr		Nb			. . .

This is not precisely the same as Mendeleev's arrangement but coincides almost completely with V. I. Spitsyn's system.

It must, however, be mentioned that in the first two decades of the 20th century the arrangement of the elements into groups was made for the most part according to Mendeleev: for example, in W. Ostwald's "The Foundations of Physical Chemistry" (1909), in Hollemann's "Textbook of Inorganic Chemistry," etc., although some authorities favored Lothar Meyer [Kallenberg "The Foundations of Chemistry" (1911), Schmidt "Inorganic Chemistry" (1911)].

Mendeleev did not term the sub-groups "main" and "secondary"; he distinguished sub-groups of odd and even series of elements and strongly emphasized the difference between them. The names he gave to the predicted elements "ekaboron," "eka-aluminum" and "ekasilicon" are a clear proof of his subdivision of the periodic system from the very beginning and not only from the major periods. There are no main and secondary sub-groups; in this sense, all the elements are equivalent with respect to their position in the periodic system. After Mendeleev's time, however, his terms "even-series" and "off-series" elements began to be replaced by the terms main and secondary. This trend shows, of course, a characteristic anthropocentrism, the division of the elements according to their significance for man in connection with the frequency of their occurrence in nature. There are obvious reasons for wanting to call the sub-group of alkali metals a main one, as also the sub-group of halogens, of carbon and silicon, etc.

In the development of knowledge regarding the elements, a further exceptionally important advance was made by the work of Moseley, and many chemists believed that the establishment of the atomic number would replace Mendeleev's law. The effect of the discovery of the atomic number on the understanding of the periodic law is shown very clearly and definitely by the following words of Prof. B. N. Nekrasov in "General Chemistry"; "...the next important stage in the development of the periodic law (1912) is associated with the work of Moseley, which both refuted and confirmed that law. The refutation was primarily of theoretical significance: since the decisive factor in atomic structure is the positive charge of the nucleus (expressed numerically by the atomic number), this should have served as the basis for the periodic system, not the atomic weight, as was assumed by Mendeleev..." No mention is made here, for example, of the fact that the isotopes of hydrogen which have the same atomic number but different atomic weights are distinguished fairly specifically chemically. Moseley's work is considered to confirm the periodic law in that the inverted positions in the sequence of the atomic weights of the pairs of elements cobalt-nickel, tellurium-iodine and argon-potassium were found to be justified from this point of view. This too is incorrect: the periodic law is confirmed both by the prediction of new elements with an exact indication of their properties and by the correction of the atomic weights.

The significance of Moseley's work should not, of course, be minimized. He gave the exact number of lanthanides and an exact indication of the number of gaps still existing in the table; in addition, the science of atomic structure was developed on the basis of his work.

The science of atomic structure, which was developed with great rapidity after the establishment of the concepts of the atomic number, again emphasized the periodicity in the position of the elements but the fact that, commencing from scandium, the introduction of electrons in the second "shell" takes place appeared to confirm that scandium and the succeeding elements differ from the preceding ones. In addition, it does not appear altogether accidental that it was the III Group (scandium or gallium) which created the uncertainty in the division of the elements into main and secondary sub-groups: precisely in that group there are no grounds for anthropocentrism. Apart from aluminum, which it is naturally desired to place in the main group, all the other members of the group are included in the infrequently-found or rare elements. Whereas the sub-groups scandium-yttrium-lanthanides and gallium-indium-thallium are distinct from each other, on the other hand, as a result of the fact that all these elements have not been closely studied, the doubt arises as to which of these sub-groups is headed by boron and aluminum and which is the secondary sub-group. But if we use D. I. Mendeleev's criterion regarding even and odd series the problem is of course resolved without any shadow of doubt and in complete agreement with the properties of the elements.

At present, however, even in textbooks for high schools, the division of the groups into sub-groups is always denoted only from the fourth period, the "main" elements being distinguished. This is the case even with L. A. Chugaev. Undoubtedly it reflects the influence of the German chemists, who attempted to dispute Mendeleev's priority and to advance that of Lothar Meyer, forgetting the main proof of Mendeleev's priority, namely the prediction of new elements.

The incorrect placing of scandium and gallium in the table of the periodic system must, therefore, be recognized as the first departure from Mendeleev's idea, the second being the replacement of the terms "even-series" and "odd-series" by the terms "main" and "secondary" sub-groups.

The similarity, pointed out by D. I. Mendeleev, between the "typical" elements, as he called them (lithium, beryllium, boron), and the elements adjacent to them in the next series (magnesium, aluminum and silicon, respectively) is also insufficiently reflected in the tables which are now published; this similarity is very well-known, particularly to analysts. This applies in part to V. I. Spitsyn's edition. In the three pairs lithium-magnesium, beryllium-aluminum, boron-silicon, the similarity is very clearly shown both in the simple bodies and in compounds, and in the reactions of the ions.

The insistence on including hydrogen in the VII Group cannot be considered as sufficiently well-founded. If we proceed from the formation of exothermic hydrides of the alkali and alkaline-earth metals, in which hydrogen behaves as an electron acceptor, not a donor, by the same token we must consider mercury to be analogous to oxygen because of the exothermic formation of an amalgam.

The time then comes to insert the pre-hydrogens into the periodic table. In his article "The chemical understanding of the ether" Mendeleev indicates that there must be an element in the zero group in the first series and that the existence of an element in the zero group in the zero series is possible. Twenty years ago I advanced the suggestion that these elements, predicted by D. I. Mendeleev toward the end of his life, might be identified with the neutron and the neutrino which were discovered long after the death of Mendeleev; similar ideas were afterwards advanced by a number of other chemists. The proposal to include the electron, positron and mesons in the periodic system can hardly be considered as correct, however, because these particles cannot be considered as chemical elements.

In connection with the representation of the periodic system the question arises of the position of the zero group in the table. The elements of this group have, of course, a dual character despite the precise determination of their properties. They may be considered both as initiating periods or as concluding them: should, for example, neon be placed in the series before sodium or in the previous series after fluorine. To join the zero group with the eighth group as was first suggested by N. A. Morozov is hardly correct, although very tempting: the zero group determines the boundary between the periods whereas the eighth is a transitional group in the middle of the periods. D. I. Mendeleev himself placed the zero group before the first group. With this arrangement the first period would contain two elements, neutron and hydrogen, the second would contain the 8 elements from helium to fluorine inclusive, the third would commence with argon and finish with bromine (i.e., it would comprise two series), and so forth; the seventh period, which together with the artificial elements contains only 13-15 members, would commence with radon. The zero period would contain only neutrino or to give it the name suggested by D. I. Mendeleev himself, "newtonium." It must be mentioned that with this arrangement the elements of the zero group become even-series (with the exception of neon) elements instead of odd-series elements.

Finally the following may be mentioned. At the heads of the groups two lines are sometimes placed (D. I. Mendeleev himself introduced these) determining the forms of the higher oxygen and hydrogen compounds, i.e., the double higher valance:

Groups	I	II	III	IV	V	VI	VII	VIII
Higher oxygen compounds	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Higher hydrogen compounds				RH_4	RH_3	RH_2	RH	

The designation was introduced long before the structure of atoms and molecules became known but it anticipated precisely that which has now become quite clear: polar oxygen compounds originate with the donation of an electron to an electronegative element whereas polar hydrogen compounds originate with the acceptance of an electron from hydrogen, i.e., in both instances with the formation of a complete octet, and the total of the valances for hydrogen and oxygen is 8. The designation of hydrogen compounds of the first three groups which is sometimes inserted is, however, an infringement of this procedure which is correct in principle:

I	II	III	IV	V	VI	VII
RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH.

In point of fact in the first groups the hydrides are formed according to the type of oxygen compounds with the donation of an electron (which is what makes certain authors insist on including hydrogen in the halogen group).

The table proposed by D. I. Mendeleev is now quite complete, it contains no gaps and its limits have been extended: the series of transuranides has been discovered and pre-hydrogens are anticipated. All this was foreseen by Mendeleev himself. Nevertheless, the table is not yet completely exhausted and many laws remain to be discovered. The science of atomic structure which has developed on the basis of the periodic law and of the concept of the atomic number has not yet given a clear answer to certain questions as to the properties of individual elements; moreover, in some instances the conclusions which result from the science of atomic structure give a less definite answer than the periodic table.

However, this much can definitely be stated: Mendeleev's principle that "the properties of the elements are a periodic function of the atomic weight" cannot be completely replaced by the new principle that "the properties of the elements are a periodic function of the atomic number (i.e., of the positive charge of the nucleus)" since the properties are determined by both these factors.*

Received June 26, 1956

Kazan State University

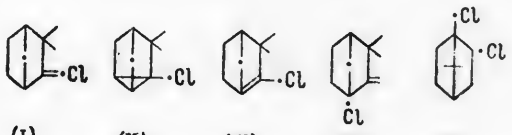
* The article was received after the author's death; some of the points mentioned in it are open to discussion.

LETTERS TO THE EDITOR

I.

My article on "The action of chlorine on camphene" was published in the Journal of General Chemistry [23, 1002 (1953)]. According to the experimental data obtained, the primary reaction products are the monochlorides (I), (II) and (III) and the dichloride (V) [J. Gen. Chem., 23, 1407 (1953)].

An article by G. Jourdoglu, Ch. Goldenberg and I. Gerarts on "The Bredt law. The 2-chloromethylcamphenilene of Tishchenko" was published in the Bulletin of the Belgian Chemical Society [66, 200 (1957)]; in this article the authors stated that the monochloride (III) corresponds to structure (IV).



(I) (II) (III) (IV) (V)

The authors of this article base their proof on the fact that the infrared absorption spectrum of the alcohol and its acetic ester, obtained from α-chlorocamphene by Meerwein and Wortmann [1], are very close to the corresponding absorption spectra of the acetate and the alcohol, obtained from the chloride (III). The authors do not supply other proofs; they do not even give the physical constants (melting point, boiling point, n_C, etc.) for their alcohol, acetic ester, the biphthalate of the alcohol, etc., which are necessary to establish their identity with the alcohol we obtained (m. p. 67-68°, melting point of the biphthalate 142-143°). The authors consider that Meerwein's chlorocamphene has structure (IV) but Meerwein himself only proposed this structure, he did not prove it. He showed that the ozonolysis of α-chlorocamphene gives chlorocamphenilone, the position of the chlorine atom not being established. α-Chlorocamphene was obtained by Meerwein by the action of phosphorus pentachloride on camphor followed by heating the camphor dichloride with phenol and anhydrous potassium acetate at 150-170°. Meerwein himself does not consider α-chlorocamphene to be an individual substance (b. p. 193-197°) and attributes structure (IV) to it on the basis of the possible analogy of its formation reaction from camphene dichloride with the conversion of isobornyl chloride into camphene. It follows, therefore, that the structure of Meerwein's α-chlorocamphene and still more so the alcohol obtained from it by the Belgian authors was in no way proven and the conclusions of these authors are unfounded.

We showed that when distilled in a fairly wide column all three monochlorides from the camphene boil within one degree; the chlorine atom in them therefore occupies a structurally equivalent position (primary I, II, III). We showed that secondary chloro-β-pinene boils at 10-12° lower than primary chloro-α-pinene, although β-pinene boils below α-pinene [2]. The difference between the boiling points of the primary chlorides (I), (II) and the tertiary chloride (IV) must be all the greater.

When its biphthalate is oxidized with potassium permanganage (2 g-at. of oxygen) our alcohol gives a diketo-alcohol $C_{10}H_{16}O_3$, whereas the alcohol with structure (IV) must give hydroxycamphenilone $C_9H_{14}O_2$; the double bond of our alcohol is, therefore, in the ring, it is not semicyclic. Finally, the chloride with structure (IV) must contain nonsponifiable chlorine, however strange this may seem at first glance, since it is both tertiary and a homolog of allyl chloride. Examples of the nonsaponifiability of a hologen atom in a tertiary position of this type are sufficiently numerous [3]: tertiary chlorides are saponified according to an ionic mechanism, the carbonium ion is planar; to obtain a planar carbonium ion in this instance requires impossibly high energies of activation; in the

great majority of instances a substitution reaction is accompanied by a Walden inversion, in this instance the latter is only possible by rupture of the bridge and closure again in the trans position, which cannot take place. Phenyl-, diphenyl- and triphenylhalogenmethanes have very mobile halogen atoms; the addition product of maleic anhydride and 9-bromoanthracene, which is both a tertiary bromide and a homolog of diphenylbromomethane, cannot, however, take part in any exchange reactions [4]: the bromine atom contained in it is also at the head of the bridge, as is the chlorine atom in the chloride (IV).

We have previously called attention to the necessity for a careful approach to the use of physical methods of investigation in organic chemistry, particularly in the chemistry, of the terpenes, where "the principle of the minimum modification of structure" is very frequently inapplicable [5]. From the above it follows that the work of the Belgian authors does not disprove the structure we proposed for the structure of the chloride (III).

D. V. Tishchenko

LITERATURE CITED

[1] Meerwein, Wortmann, Lieb. Ann. 435, 202 (1924).

[2] D. Tishchenko, B. Matveev, J. Gen. Chem. 20, 896 (1950).*

[3] See, for example, Bartlett, J. Am. Chem. Soc. 61, 3184 (1939).

[4] Bartlett, J. Am. Chem. Soc. 62, 1183 (1940).

[5] D. Tishchenko and N. Summ, J. Gen. Chem. 27, 379 (1957).*

Received June 1, 1957

II.

Our article on "The synthesis of 2,5- and 2,5'-diphenyl-hexahydro-(3,4: 3',4')-furfurans" was published in the Journal of General Chemistry 27, 1857 (1957). The compound $C_{18}H_{16}O_6N_2$, obtained by the action of nitric acid (d 1.5) in glacial acetic acid on 2,5-diphenyl-hexahydro-(3,4: 3',4')-furofuran was described by us as its dinitro derivative (pp. 1861, 1864, 1865). Recently, however, we carried out an additional investigation of the structure of this compound and showed that its oxidation leads to the formation of unsubstituted benzoic acid. In addition, we established that the compound $C_{18}H_{16}O_6N_2$ shows aldehydic reactions, and after it had been heated with dilute hydrochloric acid, nitrous acid was found in the solution.

These facts compel us to draw the conclusion that, in contrast to sesamin which, by the action of nitric acid gives an aromatic compound, 2,5-diphenyl-hexahydro-(3,4: 3'4')- furofuran is not nitrated under the conditions described by us; instead the furan ring is ruptured with the formation of aldehyde and nitrous acid ester groups, which corresponds to the composition of the compound obtained.

M. N. Shchukina
N. B. Galstukhova

* Original Russian pagination. See C. B. Translation.